ELECTRONIC STRUCTURE OF
METALLIC ALLOYS

FINAL TECHNICAL REPORT

N. H. March, J. C. Stoddart and J. S. Rousseau

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13. ABSTRACT

This two part report discusses:

a. An electron theory treatment of relaxations round the lattice of point defects in metals, and

b. the development of electron states in disordered systems by considering the electrical resistivity of liquid metals where there is strong electron scattering.

Some preliminary results are shown but applicability and generalization of this work are only suggested in this paper.

KEYWORDS:

(U) Electron Theory   (U) Scattering Theory   (U) Liquid Metals

(U) Disordered Systems   (U) Kanzaki Forces   (U) Relaxation

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Contents

Abstract.

Abstract

Since Final Report DAJA37-69-C-1223, the following papers have been published on work supported partially by this Contract:

(i)   Interaction between point defects in metals, by N. H. March and J. S. Rousseau, Crystal Lattice Defects, 2, 1-46, 1971

(ii) Partition function of a disordered system, by J. S. Rousseau, J. C. Stoddart and N H. March, J. Phys. C., 4, L59-L61, 1971

(iii) The Dirac and t matrices for spherically symmetric potentials, by J. S. Rousseau, J. Phys. C., 4, L351-L354, 1971

Furthermore, an invited paper was given at the Battelle Colloquium, Seattle last Summer on 'Computer Simulation of Lattice Defects' and will be published in the Proceedings of that meeting. This is entitled
'Kanzaki forces and electron theory of relaxation round defects'
by N. H. March and J. S. Rousseau.
The substance of this latter paper is reported in Part A of the present report.

Part B continues our work, begun by Rousseau, Stoddart and March (1970) and continued in (ii) above, on electron states in disordered systems, by considering specifically the electrical resistivity of liquid metals in the strong, as well as the weak scattering regime. While, for weak scattering, we regain the Ziman formula, we expect our theory also to apply to strong scatterers, like the liquid alkaline earth metals. Of particular interest

here are the metals calcium and barium, for which electrical

transport measurements have become available very recently

(Van Zytveld, Enderby and Collings, 1972). These workers

conclude that no simple modification of the pseudopotential theory

can explain their experiments. We report in Part B therefore

a basic theory which is capable of dealing with strong scattering

such as we encounter in these liquid metals. Calculations of

the single-centre scattering for calcium are in progress, in

order to bring our theory based on the inverse transport coefficients

into contact with experiment.

PART A

1. Introduction

Especially in metals, there has been a good deal of interest in the theory of charged defects; for example a vacancy in Cu, or Mg atoms in dilute concentrations in Li. So far, however, no very careful account of the detailed relaxations of the lattice round the defect or impurity site has been incorporated in such electron theory calculations, though attempts have been made to include some account of relaxations by modifying the Friedel sum rule, which is frequently used in defect calculations to simulate self-consistency.

The electron theory of defects in metals has proved to make interesting predictions about, for example, charged defect interactions, especially in polyvalent metals, which appear to agree in general terms with experiment (see, for example, the review by two of the present writers (March and Rousseau 1970)).

But a substantial body of work also exists in which a markedly different philosophy is adopted. Here, relaxation effects are studied as the prime objective, usually on the basis of pair forces. Unfortunately, such an approach often fails to include a proper account of electron redistribution caused by the introduction of defects or impurities into the lattice. Though this is a serious limitation, nevertheless the approach has

practical merit in that it allows local relaxations round defects to be estimated, in a way which matches these on to the correct, long-range lattice displacements given by elasticity theory, at large distances from the defect. Indeed, quite a body of work is now available giving us estimates of the displaced positions of lattice atoms about a vacancy, or a divacancy, in a number of metals.

Such calculations, made with plausible pair forces, show that even when a vacancy is created in an open body-centred cubic structure like Na metal, the atomic movements are really quite small. This is a fortunate circumstance and had been anticipated by Kanzaki (1957; see also Matsubara, 1952) in his method of lattice statics. Here, the idea is to simulate the effect of a vacancy or impurity in a lattice by regarding the originally perfect lattice as strained until it takes up the relaxed configuration appropriate to the equilibrium atomic positions in the defect lattice. Obviously, external forces must be applied to hold the other atoms in their displaced positions. We shall refer to these external forces as Kanzaki forces and to the strained, but otherwise perfect, lattice as the Kanzaki lattice. Kanzaki assumed that all the displacements $\underline{u}_\ell$, say, from the perfect lattice positions $\underline{\ell}$, were so small that one need work only to first-order in $\underline{u}_\ell$.

Thus, on the one hand, we have the electron theory, in

which a basic quantity characterizing the defect is the localized charge it displaces (as a specific example to be referred to again later, see the calculations of Stott, Baranovsky and March, 1970, on the charge displaced round vacancies in close-packed polyvalent metals) and, on the other, the method of lattice statics, with the strained Kanzaki lattice held in the relaxed final configuration by external forces.

Though the present report is concerned with the electronic structure of defects, the idea of the Kanzaki lattice will play a central role in setting up the theory. Specifically, this allows us to develop a means of treating the difference between the charge displaced by a given defect potential in the unrelaxed lattice and that displaced by the same defect potential inserted in the Kanzaki lattice. Some preliminary results for a vacancy in Cu metal are referred to, by way of illustrating the approach.

It can be objected that, to set up the Kanzaki lattice, we must know the relaxations at the outset. This is true, and we must use some starting estimates such as those referred to above from pair potential studies. However, once the charge displaced in the Kanzaki lattice by the defect potential is known, we are in a position to calculate the electric field at the ionic positions in the Kanzaki lattice, and hence from the Feynman's theorem, the Kanzaki forces. If these are not consistent with the original displacements u_ℓ, Kanzaki's method

can then be used to generate a new set of displacements.   The
new displaced charge must then be found.   Clearly, we can, in
principle, iterate until a self-consistent result is obtained.

Though, therefore, at least in principle, the theory
given here can solve the problem of the electron distribution round
a defect in a correctly relaxed lattice, there are a number of
practical issues to be resolved, which will, almost certainly,
involve major electronic computation.   Of these, a prime
problem is that, to obtain the electronic structure of a defect
centre, we must have a great deal of information about the perfect
lattice.   We do not, as yet, have that information in a suitably
explicit form for any metal but, as we shall show in section 3
below, a good deal of it, though not all, can be got from well
established methods in the band theory of perfect crystals.   The
second difficulty resides in the fact that methods of solving
the problem of scattering off a defect potential in the
unrelaxed lattice are still troublesome to apply.   However, when
both the perfect crystal, and the defect potential, can be
constructed from muffin tin potentials, we have the rigourous
one-electron theory of Beeby (1967), while for three classes of non-
muffin tin defect potentials we have available the explicit
approximations given by Stoddart, March and Stott (1969).   A
third difficulty is that we do not know precisely what potential
to take to describe the defect.   But at least, we can give
an operational definition of what that potential must be and
we do this in section 4.

We conclude this part of the report with a brief discussion of the way defect energetics might be studied within the present framework.

A convenient starting point from which to explain the basic ingredients needed in the electron theory is to study how the electron density $\rho_o(\underline{r})$ in the perfect crystal, which is accessible to experiment via the intensities of X-ray scattering at the Bragg reflections, is changed when we strain the crystal to form the Kanzaki lattice, and we turn immediately to the solution of this problem.

2. Electron density in Kanzaki lattice

We start with a perfect crystal, with atoms at lattice points We simply strain the lattice, introducing neither foreign atoms, nor vacancies.

The method we use to generate the electron density in this Kanzaki lattice is that used by Jones and March (1970, referred to subsequently as JM) in their theory of lattice dynamics. The theory is immediately useful within the framework of the Kanzaki method of lattice statics, provided only that the displacements from the sites ℓ, say $\underline{u}_\ell$, are sufficiently small so that we need work only to first-order in the displacements. This is a basic assumption of our approach, and it will have, of course, to be checked for consistency in any application. As we stressed above, however, even with a vacancy in an open structure, it is found in practice that relaxations are often quite a small fraction of the lattice parameter, and the present approach should be widely applicable.

Let the change in electron density when the lattice is 'strained' be $\rho_1(\underline{r})$. Then, to first-order in the displacements, the theory of JM allows us to write

$$\rho_1(r) = \sum_{\underline{\ell}} \underline{u}_{\underline{\ell}} \cdot \underline{R}(\underline{r} - \underline{\ell}). \qquad (2.1)$$

The vector $\underline{R}$ satisfies an integral equation given by JM which involves knowledge of the exchange and correlation energy of the inhomogeneous gas of electrons in the crystal (see Appendix . for some relevant details.) However, it is important to note that $\underline{R}(\underline{r})$ evidently also determines the gradient of the perfectly periodic lattice density $\rho_o(r)$ through

$$\nabla\rho_o(r) = \sum_{\underline{\ell}} \underline{R}(\underline{r} - \underline{\ell}). \qquad (2.2)$$

Information about $\underline{R}(\underline{r})$ in Fourier transform is therefore available at the lattice vectors $\underline{K}$. Here, in fact $R_{\underline{K}}$ is determined uniquely by the intensity of X-ray scattering at the Bragg reflections, as discussed in JM. In particular

$$\underline{R}_{\underline{K}} = i \underline{K} \rho_{\underline{K}} \qquad (2.3)$$

where $\rho_{\underline{K}}$ is the Fourier component at $\underline{K}$ of the charge density $\rho_o(\underline{r})$.

Thus, it is clear that if we know, from say a pair potential study, a first approximation to the $\underline{u}_{\underline{\ell}}$'s and if, as discussed above, these relaxations turn out to be sufficiently small, we can generate

the density $\rho_0(\underline{r}) + \rho_1(\underline{r})$ at any point in the Kanzaki lattice from a knowledge of the quantity $\underline{R}$ characteristic of the perfect lattice.

As an example to illustrate this method, we shall consider in Appendix 3 some preliminary numerical results for $\underline{R}$ in Cu metal, from which $\rho_1(r)$ for a vacancy in Cu metal can be estimated using the displacements $\underline{u}_\ell$ calculated by Tewordt (1958).

However, it is clear that, though $\rho_1(\underline{r})$ is a basic quantity needed in the theory, a good deal more information is required in order to generalize the approaches of Beeby (1967) or Stoddart, March and Stott (1969) to deal with perturbations in the Kanzaki lattice. We shall therefore turn next to discuss the Green function or density matrix describing the Kanzaki lattice. The discussion of the density above is, of course, a special case of this more general treatment. We want to emphasize though that the above discussion is exact to first-order in the displacements if the properties of the perfect lattice, as summarized in $\underline{R}(\underline{r})$, are known.

3. Green function and/or density matrix in Kanzaki lattice

We can, as we show below, set up the Green function of the Kanzaki lattice, from that of the perfect lattice, $G_o(\underline{r}\ \underline{r}'E)$ say, the latter being constructed such that the exact electron density $\rho_o\ (\underline{r}\ \underline{r}\ E_f)$, with E_f the Fermi energy, is correctly incorporated.

Below we shall work with the canonical density matrix $C_o\ (\underline{r}\ \underline{r}'\beta)$ for the perfect lattice, defined by

$$C_o(\underline{r}\ \underline{r}'\beta) = \sum_{\gamma\underline{k}} \psi^*_{\gamma\underline{k}}\ (\underline{r})\ \psi_{\gamma\underline{k}}\ (r')\ e^{-\beta\ E_\gamma(\underline{k})} \qquad (3.1)$$

where the Bloch wave functions $\psi_{\gamma\underline{k}}\ (\underline{r})$ and corresponding eigenvalues $E_\gamma\ (\underline{k})$ are generated by the periodic potential $V_p(\underline{r})$ which gives by definition the exact ground-state density in the perfect unstrained lattice.   If we take the Laplace transform of C_o with respect to β, and call the transformed variable $-E$, then we regain the Green function $G_o\ (\underline{r}\ \underline{r}'\ E)$ immediately, so that whether we work with C or G is purely a matter of mathematical convenience.

Following JM we can write for the strained lattice, a perturbing potential $\Delta V(\underline{r})$ having the form

$$\Delta\ V(\underline{r}) = \sum_{\underline{\ell}} \underline{u}_\ell \cdot \underline{P}\ (\underline{r} - \underline{\ell}). \qquad (3.2)$$

From JM,(see also Appendix 1) we know that

$$\underline{R}(\underline{r}) = \int \underline{P}(\underline{r}') \; F(\underline{r} \; \underline{r}') d\underline{r}' \qquad (3.3)$$

where F is a one-body response function given by (cf Appendix 1)

$$\frac{\partial F}{\partial E} = 2\mathrm{Re}\left[G_o(\underline{r} \; \underline{r}'E) \; \frac{\partial \rho_o}{\partial E} (\underline{r} \; \underline{r}'E) \right] \qquad (3.4)$$

where $\rho_o(\underline{r} \; \underline{r}'E)$ is the Dirac density matrix of the perfect lattice. Once the periodic potential V_p is known, ρ_o and G_o can be calculated purely from the Bloch functions $\psi_{\nu\underline{k}}(\underline{r})$ and the energies $E_{\gamma\underline{k}}$

It is clear from (3.3) that knowledge of the one-body response function $F(\underline{r} \; \underline{r}')$ plus $\underline{P}(\underline{r})$ is equivalent to knowing $R(\underline{r})$.

To generate the density matrix in the Kanzaki lattice, we now need to solve the Bloch equation

$$HC = - \frac{\partial C}{\partial \beta} \qquad (3.5)$$

where

$$H = -\tfrac{1}{2} \nabla^2 + V_p(\underline{r}) + \Delta V(\underline{r}) = H_o + \Delta V, \qquad (3.6)$$

subject to the usual delta function boundary condition $C(\underline{r} \; \underline{r}_c \; 0)$ = $\delta(\underline{r} - \underline{r}_o)$ expressing the completeness of the eigenfunctions. But H_o generates the density matrix C_o and ΔV is a perturbation, from eqn. (3.2), provided the $\underline{u}_\ell$'s are small. Thus, we can write, to first-order in ΔV (cf March, Young and Sampanthar, 1967)

$$C_{Kanzaki} (\underline{r}\ \underline{r}'\ \beta) = C_K (\underline{r}\ \underline{r}'\ \beta) \qquad (3.7)$$

$$= C_0(\underline{r}\ \underline{r}'\beta) - \int_0^\beta d\beta_1 \int d\underline{r}''\ C_0(\underline{r}\ \underline{r}''\beta - \beta_1)\ \Delta V(\underline{r}'')$$

$$C_c(\underline{r}''\ \underline{r}'\ \beta_1)$$

which determines the density matrix or Green function of the Kanzaki lattice in terms of C_0 and the perturbation ΔV, which is in turn given by eqn. (3.2).

Eqn. (3.7) is the basic result then from which we must build the solution for the defect lattice.

4. Solution for defect lattice

We now introduce the defect, and to be specific, we shall assume we create a vacancy at the origin. Let us suppose that the electron density $\rho_K(\underline{r}) = \rho_0(\underline{r}) + \rho_1(\underline{r})$ in the Kanzaki lattice changes to $\rho_f(\underline{r})$, the density in the final state containing the relaxed vacancy.

4.1 Operational definition of defect potential

We tacitly assumed above that we could generate the exact ground-state density $\rho_0(\underline{r})$, as observed say in X-ray scattering, from a one-body periodic potential $V_p(\underline{r})$: i.e.

$$\rho_0(\underline{r}) = \sum_{\gamma\underline{k}} \psi^*_{\gamma\underline{k}}(\underline{r}) \, \psi_{\gamma\underline{k}}(\underline{r}). \qquad (4.1)$$
$$(\text{occupied})$$

This essentially follows from the considerations of Kohn and Hohenberg (1964) and Kohn and Sham (1965). An operational procedure to construct $V_p(\underline{r})$ from a given $\rho_0(\underline{r})$ has been discussed rather fully by Beattie, Stoddart and March (1971).

The same argument, in essence, now enables us to define operationally the defect potential. We wish to find a potential $V_d(\underline{r})$ which, when added to the one-electron Hamiltonian H in eqn. (3.6), yields the <u>exact</u> final state density $\rho_f(\underline{r})$.

We want to stress that $V_d(r)$ is a potential to be added to H, **not** to H_0. Thus, $V_d(r)$ is generated in a system in which the ionic configurations differ only by the removal of the ion at the origin. If we had defined the defect potential as a change from H_0, all the ions would have moved and $V_d(r)$ would be a much more complex object.

For the vacancy, especially in polyvalent metals, we must not expect that the effect of $V_d(r)$ can be treated as a perturbation. The Bloch equation (3.5) with H replaced by

$$H_f = H_0 + \Delta V + V_d \ (r) \tag{4.2}$$

can again be written as an integral equation

$$C_f \ (r \ r' \ \beta) \ = C_K(r \ r' \ \beta \ ) \tag{4.3}$$

$$- \int_0^\beta d\beta_1 \int dr'' \ C_K \ (r \ r'' \beta - \beta_1) V_d(r'') \ C_f(r'' r' \beta_1)$$

where now the object C_f which is required appears also on the right-hand side of eqn. (4.3). In principle, knowing C_K from eqn. (3.7), we can obtain C_f from eqn. (4.3), with an assumed defect potential. In practice, an iterative scheme (cf. Hilton, March and Curtis, 1967) would have to be used and the procedure is certainly very lengthy and somewhat troublesome. We shall therefore consider below two approximate methods which allow us to solve (or in the second method to circumvent) the integral equation (4.3).

The idea has already been made plain.   Physically, we
anticipate that the diagonal difference $C_f(\underline{r}\ \underline{r}\ \beta) - C_K(\underline{r}\ \underline{r}\ \beta)$
$= \Delta C_{fK}$ can be usefully split into two parts, $\Delta C_{uo} = C_u(\underline{r}\ \underline{r}\ \beta)$
$- C_o(\underline{r}\ \underline{r}\ \beta)$, where C_u is the Bloch density obtained by introducing
the defect potential into the perfect lattice with Bloch density C_o,
plus another term δC taking relaxation into account.

4.2   Correction to displaced charge as calculated in unrelaxed lattice

A rough approximation to estimate δC can be given as follows.
Write, with the assumption that $V_d(\underline{r})$ varies slowly in space
(cf. eqn (3.1))

$$C_f(\underline{r}\ \underline{r}\ \beta) = C_K (\underline{r}\ \underline{r}\ \beta)\ e^{-V_d(\underline{r})} \tag{4.4}$$

and
$$C_u(\underline{r}\ \underline{r}\ \beta) = C_o(\underline{r}\ \underline{r}\ \beta)\ e^{-\beta V_d(\underline{r})} \tag{4.5}$$

Thus we have from the definitions given above

$$\Delta C_{fK} = C_K \left[e^{-\beta V_d} - 1 \right] \tag{4.6}$$

and
$$\Delta C_{uo} = C_o \left[e^{-\beta V_d} - 1 \right]. \tag{4.7}$$

Therefore it follows that

$$\delta C = \left[e^{-\beta V}d - 1 \right] \left[C_K - C_o \right]$$

$$= \left[e^{-\beta V}d - 1 \right] \Delta C_{Ko}. \tag{4.8}$$

Here then, we have a rough, but quite practicable, way of estimating the correction to the displaced charge in the unrelaxed lattice, due to relaxation, since ΔC_{Ko} is given explicitly by eqn. (3.7).

In terms of densities, we could alternatively write

$$\rho_f(\underline{r}\ E) \doteq \rho_K(\underline{r},\ E - V_d(\underline{r})\ ) \tag{4.9}$$

and

$$\rho_u(\underline{r}\ E) \doteq \rho_o\ (\underline{r},\ E - V_d(\underline{r})) \tag{4.10}$$

We stress that we only use these forms to estimate the correction to the displaced charge $\Delta\rho_{uo} = \rho_u(\underline{r}\ E) - \rho_o(\underline{r}\ E)$ due to relaxation. Then we have

$$\Delta\rho_{fK} - \Delta\rho_{uo} = \delta\rho$$

$$= \rho_K(\underline{r},\ E - V_d(\underline{r})\ ) - \rho_K(\underline{r}\ E)$$

$$- \rho_o(\underline{r},\ E - V_d(\underline{r})\ ) + \rho_o(\underline{r}\ E) \tag{4.11}$$

$$= \int d\underline{r}_1\ \Delta V\ (\underline{r}_1)\left[F\ (\underline{r}\ \underline{r}_1,\ E - V_d(\underline{r})\ ) - F(\underline{r}\ \underline{r}_1,\ E) \right]$$

which follows from the definition of the response function F. Here then is a first approximation to correct the displaced charge in the unrelaxed lattice.* Since $\Delta V(\underline{r}_1)$ is given by eqn. (3.2), it is clear that $\delta\rho$ is 0 $(\underline{u}_\ell)$, as required.

We want at this stage to comment further on the result (4.11). Through the potential $\Delta V(r)$, determined by perfect lattice properties plus the $\underline{u}_\ell$'s there is an obvious link with lattice dynamical properties. The displaced charge $\Delta\rho_{uo}$ due to $V_d(r)$ inserted into the unrelaxed lattice is to be corrected by the appropriate form (4.11): this reduces to zero, as it must, when $V_d(r) = 0$.

Around the defect, however, we need to know $F(\underline{r}\ \underline{r}_1\ E)$ as a function of E, in order to evaluate eqn. (4.11). As can be seen from eqn (3.4), this is a problem in band theory which, for a given periodic potential $V_p(r)$, is soluble by existing methods, though it will be an extensive computational task Information about the response function $F(\underline{r}\ \underline{r}_1\ E)$ will lead to progress in the field of lattice defects; another bonus one could gain then would be to map out the anisotropy of the displaced charge due to a weak perturbation, such as that due to Be in Li.

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* A more precise, but far more complicated, way of correcting the displaced charge is given in Appendix 1.

Assuming that, for a muffin tin model, $\Delta\rho_{uo}$ is found
from the theory of Beeby, or for more general potentials from the
approximation of Stoddard, March and Stott, it is clear that eqn.
(4.11) gives us an approximate method for estimating the effect
of relaxation. This then constitutes a principal result of our
report.

Actually, in the case when $\Delta V(\underline{r})$ does not vary too fast
in space, we can further simplify eqn. (4.11). In particular,
for $\rho_1(\underline{r}\ E)$ given by

$$\rho_1(\underline{r}\ E) = \int d\underline{r}_1\ \Delta V(\underline{r}_1)\ F(\underline{r}\ \underline{r}_1\ E) \tag{4.12}$$

we can then write

$$\rho_1(\underline{r}\ E) \doteq \Delta V(\underline{r}) \int d\underline{r}_1\ F(\underline{r}\ \underline{r}_1\ E) \tag{4.13}$$

The integral over $\underline{r}_1$ in eqn. (4.13) can now be carried out,
to yield

$$\rho_1(\underline{r}\ E) \doteq - \Delta V(\underline{r})\ \frac{\partial\rho_0(\underline{r}\ E)}{\partial E} = -\Delta V(\underline{r})\ \sigma_0(\underline{r}\ E) \tag{4.14}$$

where $\sigma_0(\underline{r}\ E)$ is the local density of states in the perfect
lattice. This is just the quantity Beeby (1967) calculated from
the KKR method, with the result

$$\sigma_0(\underline{r}\ E) = \frac{1}{\pi} \sum_{LL'} R_L(\underline{r}) R_{L'}(\underline{r}) \frac{1}{\tau}\ \text{Im} \int \left[\underline{t}^{-L}\ \tau G(\underline{m}) \right]^{-1}_{LL'} d\underline{m} \tag{4.15}$$

$\underline{t}$ is the t matrix for a single muffin tin potential, while all the structure dependence is in $G(\underline{m})$ for which Beeby gives explicit expressions. The integration in eqn. (4.15) is over the Brillouin zone of volume τ , while $R_L(\underline{r})$ is as usual the radial wave function. All the information needed in eqn. (4.15) is accessible through a KKR band structure calculation.

By comparing eqn. (4.14), used at the Fermi energy $E = E_f$, with the semi-empirical procedure based on eqn. (2.1), it will be interesting to see whether the approximation (4.14) is sufficiently accurate to allow $\Delta V(\underline{r})$ to be found explicitly. If so, we have, of course, through eqn. (4.14) the energy dependence of $\rho_1(\underline{r}\,E)$ required in the evaluation of eqn. (4.11), which in the approximation equivalent to eqn. (4.14) becomes

$$\delta\rho \doteqdot \Delta V(\underline{r}) \left[\sigma \ (\underline{r} \ E_f - V_a(\underline{r})) - \sigma(\underline{r} \ E_f) \right]_j. \qquad (4.16)$$

Unfortunately, though numerical calculations are in progress, results are not as yet available for ρ.

Later, when we have more knowledge of the basic response functions, refinement may be carried out via the method of Appendix 2, should it prove necessary.

If we can make the approximation that $\Delta V(r)$ is slowly varying then we find eqn. (4.14) and if we apply this at the Fermi level, we have evidently the approximate result

$$\rho_1 (\underline{r}\ E) \simeq \rho_1(\underline{r}\ E_f)\ \frac{\sigma_o(\underline{r}\ E)}{\sigma_o(\underline{r}\ E_f)} \tag{4.17}$$

Thus, in this approximation we simply scale the displaced charge below the Fermi level E_f in the Kanzaki lattice with the local density of states in the perfect crystal.

Using the first approximation for $\delta\rho$ that

$$\delta\rho(\underline{r}E) = \rho_1(\underline{r}\ E - V_d\ (\underline{r})) - \rho_1(\underline{r}\ E) \tag{4.18}$$

we see that this takes the explicit form

$$\delta\rho(\underline{r}\ E) = \rho_1\ (\underline{r}\ E) \left[\frac{\sigma_o(\underline{r}\ E \cdot V_d)}{\sigma_o(\underline{r}\ E_f)} - \frac{\sigma_o(\underline{r}\ E)}{\sigma_o(\underline{r}\ E_f)}\right] \tag{4.19}$$

and hence, at the Fermi level

$$\delta\rho(\underline{r}) = \rho_1(\underline{r}\ E_f) \left[\frac{\sigma_o(\underline{r}\ E_f - V_d) - 1}{\sigma_o\ (\underline{r}\ E_f)}\right] \tag{4.20}$$

Thus, given the local density of states $\sigma_o\ (\underline{r}\ E)$ in the perfect crystal, from the band theory calculation, the defect potential $V_d(r)$ and the displaced charge in the Kanzaki lattice at the Fermi level, we can calculate the correction to the charge displaced by V_d in the unperturbed lattice. Of course, we have only circumvented the many-electron nature of the problem by using eqn. (2.1) with $\underline{R}\ (\underline{r})$ found empirically from the Bragg reflection intensities. We stress that we can include both many-electron effects and many-body forces via the presence of $\rho_1(\underline{r})$ in the

result (4.20). But of course we are still involved in the assumption that V_d is slowly varying and we expect that refinement of the theory will lead to a form

$$\delta\rho \ (\underline{r}) = \rho_1(\underline{r} \ E_f) \ f\left[\overline{\underline{r} \ E_f}, \ V_d(\underline{r})\right] \tag{4.21}$$

The square bracket in eqn (4.20) is a first approximation to the modified function f.

4.3 Local density of states for Mg in Li

Dr. J. E. Inglesfield (private communication) has recently made preliminary calculations of the local density of states $\sigma(\underline{r}E)$ for Mg in Li and we wish to conclude this section by mentioning these results briefly.

The results are shown for two energies $\frac{1}{2} E_f$ and E_f in Figs 1 and 2. The variable used is r/r_s, where r_s is the radius of the Li atomic cell (3.265 a.u.). The Fermi energy of Li (0.173 a.u.) has been used.

The dashed curves show the original local densities of states for the pure materials, at each energy, while the solid curves show the local density of states for a Mg impurity in Li.

As Inglesfield has emphasized, something like von Laue's theorem is being recovered as we approach the Fermi energy.

It is quite clear that ...a can use the local density of states for Li thus obtained to calculate the function in the square brackets in eqn.(4.20).   Calculations are currently in progress, in conjunction with Drs. Bullough and Perrin, to obtain $\sigma_o(\underline{r}\ E)$ from Beeby's method for Li, as well as the displaced charge round an unrelaxed vacancy in this method. Eqn. (4.20) can then be used to correct for relaxation.

5. Electric field in Kanzaki lattice

Let us now consider how we can calculate the forces acting on the ions in the Kanzaki lattice from the electron theory developed above. Again, to be specific, we will consider the monovacancy, in which case a single atom has been removed from the origin. Clearly in this defect lattice, there are no forces acting on the atoms, since the relaxed configuration is in equilibrium. This implies, from Feynman's theorem, that the total electric field $\underline{E}(\underline{r})$ in the relaxed defect lattice is identically zero when $\underline{r} = \underline{\ell} + u_{\ell}$. Otherwise, there would be forces acting on the nuclei. This electric field is created by an electron density $\rho_0(\underline{r}) + \rho_1(\underline{r}) + \rho_d(\underline{r})$, plus the fields of the nuclei.

Now we put back the atom at the origin, in our vacancy example. The electron density in this Kanzaki lattice is $\rho_0(\underline{r}) + \rho_1(\underline{r})$. The electric field $\underline{E}_{Kanzaki}(\underline{r}) = \varepsilon(\underline{r})$ in this strained lattice is evidently determined by the electron density $\rho_0(\underline{r}) + \rho_1(\underline{r})$ plus the nuclear configuration. It is then clear that the <u>resultant</u> electric field acting at the nuclei must be equivalent to that due to the difference between the electron densities in the Kanzaki lattice and in the relaxed defect lattice and to the difference between the nuclear configurations.

Immediately, for the monovacancy, we see that this field must be determined by the electrostatic potential due to the

displaced electron charge round the vacancy, plus that due to
the absence of the ion at the origin. This electron density is
given by

$$\rho_f - \rho_K = \rho_d(\underline{r})$$

$$\doteq \Delta\rho_{uo} + \left[\rho_1\left(\underline{r}, E_f - V_d(\underline{r})\right) - \rho_1(\underline{r}\ E_f) \right] \quad (5.1)$$

and it is this density, together with the field of the 'absent'
ion, which determines the electric field at the ions in the
Kanzaki lattice, and hence the Kanzaki forces. From our knowledge
of potentials and displaced charges in free electron metals, it
seems that, at large $\underline{r}$, by Taylor expanding eqn. (4.16) in terms
of V_d, $\delta\rho$ will be both smaller, involving the product of $\Delta V(\underline{r})$
and V_d, and shorter range than $\Delta\rho_{uo}$, though this will have to
be verified by detailed numerical claculations. Thus at large $\underline{r}$,
we shall tentatively assume $\Delta\rho_{uo}$ to dominate in eqn. (5.1).

5.1 Some preliminary results from free electron model

However, we can readily estimate the field due to this term
$\Delta\rho_{uo}$ and it is worth recording the result here by way of
illustration. We have, from the Poisson equation

$$\nabla^2\phi = -4\pi\ \Delta\rho_{uo} \quad (5.2)$$

where ϕ is the electrostatic potential. In the case when
$\Delta\rho_{uo}$ is spherically symmetric, we find

$$r^2\ \frac{d\phi}{dr} = \int_0^r 4\pi\Delta\rho_{uo}\ (r)\ r^2\ dr \quad (5.3)$$
$$= -Q\ (r)$$

where $Q(r)$ is the total charge displaced inside a sphere of radius r. Thus we find

$$\frac{d\phi}{dr} = -\frac{Q(r)}{r^2} \, . \tag{5.4}$$

Hence, the electric field in the Kanzaki lattice (neglecting the ρ_1 terms in eqn. (5.1))is given by

$$\underline{\varepsilon} \, (\underline{r})_{\text{displaced charge}} = - \nabla\phi$$

$$= \frac{\underline{r}}{r} \frac{Q(r)}{r^2} \tag{5.5}$$

Adding on the electric field of the ion, of resultant charge Z equal to the valency, we find

$$\underline{\varepsilon} \, (\underline{r}) = \frac{\underline{r}}{r^3} \left[Q(r) - Z \right] \, . \tag{5.6}$$

For free electrons, we know asymptotically that we have the Friedel oscillations represented by

$$\Delta\rho_{\text{uo}} \sim \frac{A\cos 2k_f \, r}{r^3} \tag{5.7}$$

where k_f is the Fermi wave number.[*] We can therefore write for the asymptotic form of $Q(r) - Z$

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[*] The introduction of a phase shift, necessary for strong scattering, is easily effected.

$$Q(r) - Z \sim -\int_r^\infty \Delta\rho_{uo} \, 4\pi r^2 \, dr$$

$$= -4\pi A \int_{2k_f r}^\infty \frac{\cos t}{t} \, dt \qquad (5.8)$$

$$= 4\pi A \, Ci \, (2k_f \, r)$$

where $Ci(x)$ is the usual cosine integral, as shown. Hence we may write

$$\underline{\varepsilon} \, (\underline{r}) \sim \frac{\underline{r}}{r^3} \, 4\pi A \, Ci(2k_f \, r). \qquad (5.9)$$

An estimate of A is readily available from the work of Stott, Baranovsky and March (1970). Some results for Q(r) in Cu are shown in Fig 3. Hence, if we assume this electric field, evaluated at the atomic positions in the Kanzaki lattice, acts on the resultant ionic charge Ze at each site, we have a first estimate of the Kanzaki forces as Ze $\underline{\varepsilon}(r)$.

We want to emphasize that this is only a very crude example. It **will** be necessary to estimate the contribution due to ρ_1 in eqn. (5.1) as well as to calculate $\Delta\rho_{uo}$ beyond a free-electron model. In both calculations, we need the perfect lattice solutions. Work is in progress to evaluate the displaced charge $\Delta\rho_{uo}$ in Li for a mono-vacancy in the unrelaxed lattice, from the theory of Beeby (1967), but results are not, as yet, available. However, Harris (1968) has already successfully applied Beeby's method to the impurity problem. Since the Beeby theory is based on the KKR method, the necessary response functions are already

contained in the KKR solutions for the perfect lattice.   Thus
we have here a basis for a rather precise evaluation of the
displaced charge in the relaxed defect lattice.

Once the electric field is known, the Kanzaki forces can be
found and Kanzaki's original method used to obtain a new set of
displacements.

6. <u>Kanzaki forces and energies of mono- and divacancy</u>

As a further illustration of the present approach, let us
try to get the Kanzaki forces associated with a Hartree treatment
of a vacancy in a metal.   Then we can write for the total energy
of the metal

$$U = -\tfrac{1}{2} \int d\underline{r} \left[\nabla^2_{\underline{r}} \, \rho(\underline{r}\, r') \right]_{\underline{r}' \,=\, \underline{r}} + \tfrac{1}{2} \int d\underline{r} \; d\underline{s} \, \frac{\rho\,(\underline{r})\,\rho(\underline{s})}{\}\underline{r} - s \}}$$

$$+ \int d\underline{r} \; \rho(\underline{r}) \; \psi\,(\underline{r}) + \Phi \tag{6.1}$$

The first term in eqn. (6.1) is the kinetic energy, the second
is the classical electron-electron interaction energy, the third is
the interaction energy of the conduction electrons with the ion
cores, while Φ represents the core-core interaction energies.

As the present writers have argued, the energy can be written
when the metal is deformed, in terms of the components of the
displacement field as

$$U = U_o + \tfrac{1}{2} \sum_{\ell\,\ell'\,\alpha\beta} A_{\ell\ell'\alpha\beta} \; \xi_{\ell d} \; \xi_{\ell'\beta} \tag{6.2}$$

and if, at the same time, the lattice is subject to external _orces,
then the following term

$$K = - \sum_{\ell\alpha} F_{\ell\alpha} \; \xi_{\ell\alpha} \tag{6.3}$$

must be added to eqn. (6.2) where $F_{\ell\alpha}$ are the Kanzaki force
components.

If we assume the existence of a pseudoatom, then we can write

$$-\sum_{\ell\alpha} F_{\ell\alpha} \xi_{\ell\alpha} = E_{pseudoatom} + \int d\underline{r}\, \Delta(\underline{r}) \left[V(\underline{r}) - \psi(\underline{r}) \right]$$
$$- \int d\underline{r}\, \rho_{V}(\underline{r})\, \psi(\underline{r}) \tag{6.4}$$

where

$$\psi(\underline{r}) = \sum_{\ell} \psi(\underline{r} - \underline{\ell}). \tag{6.5}$$

It will clearly be of interest to see whether the above approximation to the Kanzaki forces gives results similar to those of the previous section, based on direct calculation of the electric field at the ions.

The interest in the above calculation resides in its possible extension to estimate directly the effects of relaxation on the divacancy binding energy. Unfortunately, it is then necessary not only to know how the displaced charge round the two-centre problem is related to that round the one-centre problem[*], but also it is necessary to relate the positions of the relaxed atoms round a monovacancy to those when the second vacancy is brought up to the near-neighbour distance.

We want to conclude, because of the difficulty of this problem, by pointing out a possible approach related again to calculating the electric field $\underline{E}(\underline{r})$ in the final equilibrium configuration.

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[*]Such a calculation for an impurity-vacancy complex in a metal was carried out by Alfred and March (1957). For a divacancy, it is practicable to find the displaced charge from the model of Seeger and Bross (1956).

We have, for a system in equilibrium under Coulomb forces, with kinetic energy T and potential energy U,

$$2T + U = 0. \tag{5.6}$$

But when forces are required to hold two defects at distance a, we can write

$$2T + U = - a \frac{dE}{da} \tag{6.7}$$

This equation can be integrated with respect to a to yield, since $T + U = E$

$$a^2 E(a) = \int_a^\infty R \, U(R) dR. \tag{6.8}$$

Thus, if the potential energy U(R) can be obtained as a function of R, we could obtain the interaction energy as a function of distance. Certainly in a Hartree framework, the calculation of U(R) is then a problem in electrostatics, knowing the $\underline{u}_\ell$'s and the density $\rho_o(r) + \rho_1(\underline{r}) + \rho_d(\underline{r})$ in the final equilibrium state.

We want, however, to make the point that R in equ.. (6.8) is really to be restricted to lattice separations between the vacancies and is not therefore a continuous variable.

We conclude that, unless the use of pair potentials can be justified, which is unlikely round a divacancy in a polyvalent metal, it is going to be of considerable interest to map out the electric field $\underline{E}(\underline{r})$ (zero at $\underline{r} = \underline{\ell} + \underline{u}_\ell$) in the final state, and find the associated energy stored in the field. We suspect that (6.7) ought eventually to be replaced by difference equations in an exact formulation.

We turn finally to discuss how the energy in the Kanzaki
lattice might be calculated within the present framework.

Let T_K and U_K be the kinetic and potential energies in the
Kanzaki lattice, for a given separation R between the two vacancies.
Then we can write

$$2\,T_K + U_K = -\sum_{\underline{\ell}} (\underline{\ell} + \underline{u}_\ell) \cdot \underline{F}_\ell \tag{6.9}$$

where the $\underline{F}_\ell$'s are the Kanzaki forces. Naturally, those forces,
and also the displacements $\underline{u}_\ell$ depend on the separation R.

In one-body potential theory as used in this paper, where
an attempt is made to incorporate some of the many-body effects
into the potential, it seems best to relate the total energy to
the potential energy since at least the classical part of this
is calculable from the electron density plus the potential of the
nuclear framework. Thus we can write the above equation in the form

$$E_K(R) + U_K(R) = -\sum_{\ell} (\underline{\ell} + \underline{u}_\ell) \cdot \underline{F}_\ell \tag{6.10}$$

Evidently, from the electron density and the electric field $\underline{\varepsilon}(\underline{r})$
we can calculate $E_K(R)$ and $E_K(\infty)$, the difference giving us a
part of the relaxation energy. Naturally $E_K(\infty)$ involves
crucially the displacements around a single vacancy, while $E_K(R)$
involves those round a divacancy.

If X-ray scattering experiments could be refined to yield
not only the electron density $\rho_o(r)$ in the perfect crystal, but
the density around an impurity or an imperfection, band theory
would allow the construction of the crystal potential $V_p(r)$ and
the defect potential $V_d(r)$. Until such time as that becomes
possible, we must use the best available methods, based on
refinements of Slater $\rho^{\frac{1}{3}}$ exchange to construct these potentials
so as to incorporate at least some part of the electron-electron
interactions.

Knowing starting displacements $\underline{u}_\ell$, $\rho_1(\underline{r})$ can be estimated
semi-empirically from eqn. (2.1) at the Fermi level. Further-
more its energy dependence is accessible through the approximate
result (4.14) in terms of the local density of states in the
perfect crystal. The charge displaced in the Kanzaki lattice by
the defect potential $V_d(\underline{r})$ can then be estimated from that
displaced by V_d inserted in the unrelaxed lattice, corrected by
eqn. (4.16). This displaced charge can then be used to find
the Kanzaki forces and hence to calculate a new set of displacements.

Finally, it is emphasised that, within the present framework,
calculations of defect energies should be attempted from the
classical potential energy terms, plus, if necessary, estimates
of the exchange energy from the electron density. The kinetic

energy should not be calculated, however, from the density matrices discussed in this report, for these have incorrect off-diagonal elements, though the diagonal elements agree with the correct many-body density matrix.

Part B

7. Introduction

In earlier reports (see also Rousseau, Stoddart and March, 1970; 1971) we developed a density matrix theory of electron states in disordered systems and we applied it specifically to calculate the electronic density of states in liquid Be. Our conclusion was that the dip in the density of states in crystalline Be, resulting from the band overlap which explains its metallic character, is only partially 'filled in' on melting. We argued that, to describe this effect, we needed a strong scattering theory, and that was developed in our earlier work.

To bring such a theory into direct contact with experiment is at present difficult. Although, in principle, photoemission experiments on liquid Be ought to reflect the density of states, it is true at present that the most direct contact with experiment is through the electrical transport coefficients. We therefore develop here a theory of the electrical resistivity. The motivation for the present approach is provided by the theory of inverse transport coefficients, pioneered by Edwards (1965). This theory is therefore discussed first, in its general form, and subsequently single-centre approximations to the density matrix are made, in order to make progress in the calculation of the resistivity. Finally, a method of calculating single-centre density matrices from radial wave functions is presented. Numerical calculations based on this approach are in progress.

8.   An exact formula for the electrical resistivity

The derivation which follows closely resembles Greenwood's (1958) treatment which led to an exact expression for the conductivity.   The final form for the resistivity bears a strong resemblance to an expression obtained by Edwards (1965).   We show that Edwards' result needs modifying, however, in the denominator term.

Consider a Hamiltonian

$$H(t) = \frac{1}{2m} \left\{ \left(\frac{\hbar}{i} \frac{\partial}{\partial x} + eFt \right)^2 + \left(\frac{\hbar}{i} \frac{\partial}{\partial y} \right)^2 + \left(\frac{\hbar}{i} \frac{\partial}{\partial z} \right)^2 \right\} \quad (8.1)$$

$$+ \Phi(x+ct,y,z)$$

where the vector potential $(-eFt,0,0)$ corresponds to an electric field $(F,0,0)$ and the potentials of the system, giving rise to the total potential Φ as

$$\Phi(\underline{r}) = \overline{\sum_i \phi(\underline{r}-\underline{R}_i)} \qquad (8.2)$$

are all moving with velocity $(-c,0,0)$.   If c is small, then we may write

$$\Phi(x+ct) \approx \Phi(x) + ct \frac{\partial}{\partial x} \Phi(x) \qquad (8.3)$$

and so

$$H(t) = H_o(t) + ct \frac{\partial \Phi}{\partial x} \qquad (8.4)$$

where H_o is got by putting $c = 0$ in (8.1), and is in fact equal to the Hamiltonian used by Greenwood (1958). He proves that

$$H_o(t) = \exp(-ieFtx/\hbar)H_o(0)\exp(ieFtx/\hbar) \qquad (8.5)$$

and so from

$$H(t) = \exp(-ieFtx/\hbar)H(0)\exp(ieFtx/\hbar) + ct\, \Phi' \qquad (8.6)$$

where $\Phi' = \partial\Phi/\partial x$, and $H(0)$ is the Hamiltonian at $t = 0$, which is the Hamiltonian of the unperturbed system. Obviously, H will have an eigenvalue equation of the term

$$H(t)\Psi(t) = E(t)\Psi(t) \qquad (8.7)$$

and if one takes

$$\Psi_n(t) = \psi_n \exp(-ieFtx/\hbar) \qquad (8.8)$$

where $\psi_n = \psi_n(0)$, it can easily be seen that the eigenvalues in (8.7) are equal to

$$E_n(t) = E_n + {}^c t\Phi'_{nn} \qquad (8.9)$$

where

$$\Phi'_{nn} = \int d\underline{r}\; \psi_n^*(\underline{r})\; \Phi'\; \psi_n(\underline{r}) \qquad (8.10)$$

But Φ'_{nn} as defined in (8.10) is just the expectation value of the force on an electron in the state n in the absence of any electric field, and hence is zero.

The equation of motion for the density matrix ρ is

$$i\hbar\, \frac{d\rho}{dt} = [H\rho] \qquad (8.11)$$

Substituting this into the equation of motion for the matrix elements of ρ, i.e.

$$\frac{d}{dt}\, \rho_{nm} = (n|\frac{d\rho}{dt}|m) + (\frac{dn}{dt}\,|\rho|m) + (n|\rho| \quad \qquad (8.12)$$

and using the standard result

$$(m|\,\frac{dn}{dt}) = \frac{-(m\,|\,\frac{dH}{dt}\,|\,n)}{(E_m - E_n)} \qquad (8.13)$$

we arrive at the result

$$\rho_{nn} = f_n \qquad (8.14)$$

where $f_n = f(E_n)$, the Fermi function for energy E_n, and

$$g_{nm} = -\pi\hbar[eFv_{nm} + c\Phi'_{nm}]\,\left(\frac{df}{dE}\right)_{E_n}\,\delta(E_n - E_m) \qquad (8.15)$$

where we have written $\rho = f + g$, and worked to first order in F or c throughout. Also,

$$v_{nm} = \frac{\hbar}{im}\int d\underline{r}\;\psi_n^*\,(\underline{r})\,\frac{\partial}{\partial x}\,\psi_m(\underline{r}) \qquad (8.16)$$

i.e. v_{nm} is the velocity matrix element.

The Hamiltonian which we have used (equation (8.1)) corresponds to a physical situation where the coordinate axes are translated with uniform velocity c down the electric field. If we make c equal to the drift velocity, then we are in a position to calculate the force on an electron, which of course

must vanish, since a steady state has been established by

and   Hence

$$-\sum_{nm} \rho_{nm} \, \Phi'_{mn} + eF \sum_{n} \rho_{nn} = 0 \qquad (8.17)$$

for c equal to the drift velocity. Neglecting oscillating terms,
we get the resistivity R to be

$$R = -\frac{2\pi\hbar}{\Omega\rho_e^2} \, e^2 \sum_{nm} \Phi'^2_{nm} \left(\frac{df}{dE}\right)_{E_n} \delta(E-E_n) \qquad (8.18)$$

$$\left\{ 1 + \frac{2\pi\hbar}{\Omega\rho_e} \sum v_{nm} \, \Phi'_{mn} \left(\frac{df}{dE}\right)_{E_n} \delta(E_n - E_m) \right\}^{-1}$$

Eqn (8.18) can be written in terms of the energy derivative of the Dirac
matrix ρ' where

$$\rho'(\underline{rr}'E) = \sum_{n} \psi_n^*(\underline{r}) \psi_n(\underline{r}') \delta(E-E_n) \qquad (8.19)$$

and the result is

$$R = N/(1+D) \qquad (8.20)$$

where

$$N = -\frac{2\pi\hbar}{\Omega\rho_e^2} \, e^2 \int_0^\infty dE \, \frac{df}{dE} \int d\underline{r}_1 \, d\underline{r}_2 \, \frac{\partial\Phi(\underline{r}_1)}{\partial x_1} \, \frac{\partial\Phi(\underline{r}_2)}{\partial x_2} \qquad (8\ 21)$$

$$| \rho'(\underline{r}_1\underline{r}_2 \, E)|^2$$

and

$$D = \frac{2\pi\hbar^2}{\Omega i m \rho_e} \int_0^\infty dE \frac{df}{dE} \int d\underline{r}_1 d\underline{r}_2 \frac{\partial \Phi(\underline{r}_2)}{\partial x_2} \rho'(\underline{r}_1\underline{r}_2 E) \frac{\partial}{\partial x_1} \rho'(\underline{r}_2\underline{r}_1 E)$$

(8.22)

where Ω is the total volume, and ρ_e the mean electron density.
The term N is, apart from multiplying factors, the same as Edwards
(1965) finds, but the denominator term D is different, in that it
contains $\rho'(\underline{r}_1\underline{r}_2 E)$, whereas Edwards' result replaces this by
$G^+(\underline{r}_1\underline{r}_2 E)$. It is not correct to say (as Edwards has done) that
G^+ contains terms involving $[E-E_n]^{-1}$, which are related to the
virial. Further, it is easy to see that (8.22) is real, whereas
Edwards' denominator would give rise to a complex resistivity.

The exact expression for the resistivity is given by (8.20) and
is the basic result in this section. We proceed now with an
analysis of this formula, to obtain a form which is amenable to
numerical evaluation. From this point we work in atomic units
$e = \hbar = m = 1$.

9. Representation for the Dirac matrix ρ'

To enable the ensemble average to be performed in equation
it is useful to consider a representation for the Dirac matrix in the
form,

$$\rho'(\underline{r}+\underline{x},\underline{r},E) = \rho'_0(x,E)\prod_1 \left(1+\underline{f}(\underline{r}-\underline{t}_1, \underline{x}, E)\right)$$

(9.1)

where ρ_0' is the free particle matrix,

$$\rho_0' \; (x,E) = \frac{\sin(x/2E)}{2\pi^2 x} \tag{9.2}$$

The dynamical equation for ρ' is

$$-\tfrac{1}{2} \nabla_{\underline{x}}^2 \; \rho'(\underline{r}+\underline{x},\underline{r},E) = \left(E - \sum_\alpha \phi(\underline{r}+\underline{x}-\underline{t}_\alpha) \right) \rho'(\underline{r}+\underline{x},\underline{r},E) \tag{9.3}$$

and substitution of (9.1) into (9.3) leads to an equation for f in the form,

$$\left[-\tfrac{1}{2}\nabla_{\underline{x}}^2 - \frac{\left(\nabla_{\underline{x}}\rho_0'(x,E) \right)}{\rho_0'(x,E)} \cdot \nabla_{\underline{x}} + \phi(r+\underline{x}-\underline{t}_\alpha) \right] f(\underline{r}-\underline{t}_\alpha, \underline{x}, E)$$

$$+ \phi(\underline{r}+\underline{x}-\underline{t}_\alpha) - \tfrac{1}{2}\sum_{\substack{b\\(\neq\alpha)}} \frac{\left(\nabla_{\underline{x}} \cdot f(\underline{r}-\underline{t}_\alpha,\underline{x},E) \right)\left(\nabla_{\underline{x}} \cdot f(\underline{r}-\underline{t}_b,\underline{x},E) \right)}{1 + f(\underline{r}-\underline{t}_b, \underline{x}, E)} = 0 \tag{9.4}$$

We now make the basic assumption that $f(\underline{r}-\underline{t}_x, \underline{x},E)$ is a localized function in $\underline{r}$-space, centred around the site $\underline{t}$. The last term in (9.4) is then obviously an overlap term between functions f centred on different sites. If the f's are sufficiently well localized we may neglect this term, and the resulting equation for f may be readily solved to give,

$$f(\underline{r},\underline{x},E) = \frac{\rho_L' \ (\underline{r}+\underline{x},\underline{r},E) - \rho_O' \ (x,E)}{\rho_O' \ (x,E)} \qquad (9.5)$$

The matrix ρ_L' is the 'local' Dirac matrix determined by the local potential ϕ representing one of the scattering centres, and satisfies,

$$\left(-\tfrac{1}{2} \ \nabla_{\underline{x}}^2 + \phi(\underline{r}+\underline{x}) - E\right) \rho_L' \ (\underline{r}+\underline{x},\underline{r}, \ E) = 0 \qquad (9.6)$$

Alternatively, in terms of wave-functions we have,

$$\rho_L' \ (\underline{r}+\underline{x},\underline{r},E) = \sum_n \psi_n^*(\underline{r}+\underline{x})\psi_n(\underline{r})\delta(E-E_n) \qquad (9.7)$$

where the ψ_n satisfy the Schrödinger equation with potential ϕ and eigenvalue E_n.

The final representation for ρ' is then given by (9.1) with f determined by (9.5).

10. The Ensemble Average

We focus attention first upon the numerator of the expression (8.20) for the resistivity, leaving the denominator term for later investigation. To obtain the correct ensemble average for P we must of course average both terms together, but this is likely to prove difficult and will be postponed for the present.

Substitution of (8.1) into the numerator N of (8.20) gives after some re-arrangement of factors,

$$\langle N \rangle = \frac{2\pi}{\rho_e^2 \Omega} \int dE \ f'(E) \int d\underline{r}_1 \ d\underline{r}_2 \ \left(\rho'_o(\underline{r}_1 - \underline{r}_2, E) \right)^2 \tag{10.1}$$

$$x \frac{\partial}{\partial \alpha} \cdot \frac{\partial}{\partial \beta} \left\langle \prod_i \left(1 + f_{\alpha\beta} \ (\underline{r}_1 - \underline{t}_i, \ \underline{r}_2 - \underline{t}_i, \ E) \right) \right\rangle_{\alpha=\beta=0}$$

where.

$$f_{\alpha\beta}(\underline{r}_1, \underline{r}_2, E) = \left(1 + \hat{f}(\underline{r}_1 \underline{r}_2 E) \right) \left(1 + f(\underline{r}_2 \underline{r}_1 E) \right)$$

$$\exp\left\{ \alpha \frac{\partial \phi(\underline{r}_1)}{\partial x_1} + \beta \frac{\partial \phi(\underline{r}_2)}{\partial x_2} \right\} - 1 \tag{10.2}$$

The major difficulty in the evaluation of the ensemble average in (10.1) is lack of knowledge of the n-body ionic correlation functions, only the two-body correlation function being reasonably well known.

We may obtain immediately the result for a random system from (10.1) as in this case the correlation functions are of course known exactly. We obtain (see .Rousseau, Stoddart and March, 1970)

$$\langle N \rangle_R = \frac{2\pi}{3\rho_c^2 \Omega} \int dE f'(E) \int d\underline{r}_1 d\underline{r}_2 \ \left(\rho'_o(\underline{r}_1 - \underline{r}_2, E) \right)^2 F_R(\underline{r}_1 - \underline{r}_2, E) \tag{10.3}$$

where

$$F_R(\underline{r}_1 - \underline{r}_2, E) = \left[\rho \int d\underline{x} \left(\nabla_{\underline{r}_1} \phi(\underline{r}_1 - \underline{x}) \right) \left(\nabla_{\underline{r}_2} \phi(\underline{r}_2 - \underline{x}) \right) k_L(\underline{r}_1 - \underline{x}, \underline{r}_2 - \underline{x}, E) \right.$$

$$\times k_L(\underline{r}_2 - \underline{x}, \underline{r}_1 - \underline{x}, E)$$

$$+ \rho^2 \int d\underline{x} \left(\nabla_{\underline{r}_1} \phi(\underline{r}_1 - \underline{x}) \right) k_L(\underline{r}_1 - \underline{x}, \underline{r}_2 - \underline{x}, E) k_L(\underline{r}_2 - \underline{x}, \underline{r}_1 - \underline{x}, E)$$

$$\left. \int d\underline{y} \left(\nabla_{\underline{r}_2} \phi(\underline{r}_2 - \underline{y}) \right) k_L(\underline{r}_1 - \underline{y}, \underline{r}_2 - \underline{y}, E) \times k_L(\underline{r}_2 - \underline{y}, \underline{r}_1 - \underline{y}, E) \right]$$

$$\times \exp\left\{ \rho \int d\underline{x} \left[k_L(\underline{r}_1 - \underline{x}, \underline{r}_2 - \underline{x}, E) k_L(\underline{r}_2 - \underline{x}, \underline{r}_1 - \underline{x}, E) - 1 \right] \right\}$$

$$(10.4)$$

and

$$k_L(\underline{r}_1 \underline{r}_2 E) = \frac{\rho_L'(\underline{r}_1, \underline{r}_2, E)}{\rho_o'(\underline{r}_1 - \underline{r}_2, E)} \qquad (10.5)$$

The ensemble average appropriate to a liquid metal may also be performed on (10.1) using the approximate n-body ionic correlation functions proposed by Rousseau, Stoddart and March (1970). However in this case the result is increased considerably in complexity and we can see no way of using it constructively at the present time. This expression for the liquid metal average $< N>_L$ takes the same general form as the random average result (10.3) with F_R replaced by a function of $\underline{r}_1 - \underline{r}_2$ which contains information about the ionic correlation through the two-body correlation function, if we use the approximations proposed by Rousseau, Stoddart and March. Even if the exact correlation functions were used to perform the average, the

result for $< N >$ would retain the same structure as (10.3)
with F_R replaced by a function involving these exact correlation
functions. However, even the crudest approximation to these
functions seems to lead to an intractable result for $< N >$
and we will consider here only the random average result (10.3).
We propose later that an approximate account of structure can
be taken simply through the liquid structure factor $S(q)$
in a manner identical to that in the usual pseudopotential
formulation (Ziman, 1961).

11. The Weak Scattering Limit

To $0(\phi^2)$ the denominator in (8.20) does not
contribute and we obtain from (10.3) and (10.4)

$$R = \frac{2\pi}{3\rho_e^2 \Omega} \int dE f'(E) \int d\underline{r}_1 \, d\underline{r}_2 \left(\rho_0^i(\underline{r}_1 - \underline{r}_2, E) \right)^2 F_R^{(2)} (\underline{r}_1 - \underline{r}_2, E)$$

$$(11.1)$$

where

$$F_R^{(2)} (\underline{r}_1 - \underline{r}_2, E) = \rho \int d\underline{x} \left(\nabla_{\underline{r}_1} \phi(\underline{r}_1 - \underline{x}) \right) \left(\nabla_{\underline{r}_2} \phi(\underline{r}_2 - \underline{x}) \right) \cdot \quad (11.2)$$

If we define the Fourier transform $\tilde{\phi}(f)$ by

$$\phi(\underline{r}) = \frac{1}{(2\pi)^3} \int df \, e^{if \cdot \underline{r}} \, \tilde{\phi}(f) \qquad (11.3)$$

and use

$$\rho_0^i (\underline{r}_1 - \underline{r}_2, E) = \frac{1}{(2\pi)^3} \int d\underline{k} \, e^{-i\underline{k}(\underline{r}_1 - \underline{r}_2)} \delta(E - (k^2/2))$$

$$(11.4)$$

then we obtain.

$$F_R^{(2)}(\underline{r}_1 - \underline{r}_2, E) = \frac{\rho}{(2\pi)^3} \int d\underline{p} \; p^2 \; e^{i \; \underline{p} \cdot (\underline{r}_1 - \underline{r}_2)} \; |\tilde{\phi}(\underline{p})|^2 \quad (11.5)$$

and through

$$R = \frac{\rho}{12\pi^3 \rho_e^2} \int_0^{2k_f} dq \; q^3 \; |\tilde{\phi}(q)|^2 \quad (11.6)$$

This result is the well known Ziman formula for the resistivity if we regard $\tilde{\phi}(\underline{q})$ as the Fourier transform of the pseudopotential describing the interaction between an electron and a single screened ion. It may be shown that an equivalent result can be obtained from the numerator N in the liquid metal case, the only change being the replacement of the potential part of (11.6) with $S(q) |\tilde{\phi}(q)|^2$ where $S(q)$ is the structure factor.

12. Definition of Pseudopotential

The single ion potential cannot be regarded as a perturbation and we require an evaluation of the complete term (10.3). We work with the random average result which can be put into an interesting form if we define $\tilde{F}(\underline{k}, E)$ by.

$$F_R(\underline{r}_1 - \underline{r}_2, E) = \frac{1}{(2\pi)^3} \int d\underline{k} \; e^{i\underline{k} \cdot (\underline{r}_1 - \underline{r}_2)} \; \tilde{F}_R(\underline{k}, E). \quad (12.1)$$

If we write $\tilde{F}$ in the form,

$$\tilde{F}_R(\underline{k},E) = \rho k^2 A_R(\underline{k}) \tag{12.2}$$

then comparison with (11.5) and the derivation of the weak scattering result shows that if we consider the numerator as giving the whole resistance then we have,

$$\dot{R} = \frac{\rho}{12\pi^3 \rho_e^2} \int_0^{2k_f} dq \; q^3 A_R(q). \tag{12.3}$$

To second order in ϕ we have of course,

$$A^{(2)}(q) = |\tilde{\phi}(q)|^2 \tag{12.4}$$

but in the general case (10.4) can be used to define $A_R(q)$. We obtain an equivalent result for the liquid metal, the contribution of the numerator taking exactly the same form as (12.3). However in this case the appropriate transform $A_L(q)$ depends on both the local ionic potential ϕ and the ionic correlation functions.

We have therefore the interesting result that if the numerator N is the dominant contribution then the resistance takes exactly the same form as the weak scattering result (11.6) We may use $A_R(q)$ therefore to define a local 'pseudopotential' $V(r)$ through

$$A_R(q) = |\tilde{V}(q)|^2 \tag{12.5}$$

in the usual sense as that potential which gives the correct
scattering phase shifts in Born approximation.   In the liquid
metal case it is obvious that this 'pseudopotential' will depend
on the structure, although in a first approximation one may take
the potential $V(r)$ from the random average result and include
structure simply by use of $A_R(q)S(q)$ in place of A_R.   A structure
'pseudopotential' arises in the formulation of Rubio (1969) and
has been calculated by Ashcroft and Schaich (1970).   However
Rubio's result for R is correct only to lowest order in $(k_f \ell)^{-1}$
where ℓ is the mean free path of an electron at the Fermi surface.
The theory presented here is free from such limitations.

13. The Denominator Term

The ensemble average of D given by (8.22) can be performed
in a similar way to that of N.   However we use here the
additional representation,

$$\frac{\partial \rho' (\underline{r}_1, \underline{r}_2, E)}{\partial x_i} = \frac{\partial \rho_0' (\underline{r}_1 - \underline{r}_2, E)}{\partial x_i} \prod_\alpha m(\underline{r} - \underline{t}_\alpha, \underline{r}_2 - \underline{t}_\alpha, E) \tag{13.1}$$

where, again neglecting overlap terms,

$$m(\underline{r}_1, \underline{r}_2, E) = \frac{\partial \rho_L' (\underline{r}_1 \underline{r}_2 E)}{\partial x_i} \Bigg/ \frac{\partial \rho_0' (\underline{r}_1 - \underline{r}_2, E)}{\partial x_i} \tag{13.2}$$

The final result for the random average is

$$\langle D \rangle_R \cong - \frac{2\pi i \rho}{\rho_e \Omega} \int dE \; f'(E) \int d\underline{r}_1 d\underline{r}_2 \int d\underline{y} \; \frac{\partial \phi(\underline{r}_1 - \underline{y})}{\partial x_1} \; \rho'_L(\underline{r}_1 - \underline{y}, \underline{r}_2 - \underline{y}, E)$$

$$\times \; \frac{\partial \rho'_L (\underline{r}_2 - \underline{y}, \underline{r}_1 - \underline{y}, E)}{\partial x_1} \qquad (13.3)$$

where terms of higher order in ρ have been omitted. To obtain the correct ensemble average for R we must of course average both N and D together. However a sufficiently good approximation will probably be given by

$$\langle R \rangle = \frac{\langle N \rangle}{1 + \langle D \rangle} \qquad * \qquad (13.4)$$

The interesting possibility then arises that in certain circumstances (if the scattering is sufficiently strong) we could get $1 + \langle D \rangle \to 0$, representing a transition to an insulating state. However this point requires further investigation, and we will focus attention here on the contribution of N to the resistance.

14. Proposed Computational Scheme

We propose a computational scheme based upon the result (12.3) for the resistance, but including the effect of structure through the introduction of the liquid structure factor $S(q)$. Thus we have approximately,

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* An improved approximation is $\langle R \rangle = \langle N \rangle - \frac{\langle ND \rangle}{1 + \langle D \rangle}$ which reduces to (13.4) if $\langle ND \rangle = \langle N \rangle \langle D \rangle$.

$$R = \frac{\rho}{12\pi^3 \rho_e^2} \int_0^{2k_f} dq\; q^3\; A_R(q)\; S(q) \qquad (14.1)$$

in which therefore the random ensemble average of N is used to
define a 'pseudo-potential' according to (12.5)   The structure
enters through $S(q)$ in a manner identical to that in the standard
pseudopotential form for R.

A further simplification is assumed in the formula
for the resistance in the first calculations.   We obtain $A_R(q)$
from the Fourier transform of the first term only in (10.4)
neglecting the effect of the exponential term.   Thus using (10.5)
we take

$$F_R(\underline{r}_1 - \underline{r}_2, E) = \rho \int d\underline{x} \left(\nabla_{\underline{r}_1} \phi(\underline{r}_1 - \underline{x}) \right) \left(\nabla_{\underline{r}_2} \phi(\underline{r}_2 - \underline{x}) \right) \qquad (14.2)$$

$$\frac{\left| \rho_L'\; (\underline{r}_1 - \underline{x}, \underline{r}_2 - \underline{x}, E) \right|^2}{\left(\rho_o'\; (\underline{r}_1 - \underline{r}_2, E) \right)^2}$$

where $A_R(q)$ is determined by (12.1) and (12.2) .   Equation (14.2)
is just the term of $O(\rho)$ in an expansion of F_R in powers of the
ionic density.   What we are essentially assuming is that the
'pseudopotential', which is defined in terms of A_R by (12.5)
does not have any explicit dependence on the ionic density.
We turn finally to discuss the single-centre scattering, defined
through ρ_L.

15. Single centre scattering

The potential is assumed to be spherically symmetric.

15.1 The t-matrix   Its integral equation is

$$t(\underline{x},\underline{y}) = v(\underline{x})\delta(\underline{x}-\underline{y}) + \int d\underline{z} \; v(\underline{x}) \; G_o(\underline{x} - \underline{z})t(\underline{z},\underline{y}) \quad (15.1)$$

$v(\underline{x})$ is the single centre potential and

$$G_o^{\pm}(\underline{r}-\underline{r}') = -(4\pi)^{-1} \exp[\pm ik | \underline{r}-\underline{r}' |][| \underline{r}-\underline{r}' |]^{-1} \quad (15.2)$$

where $k = E^{\frac{1}{2}}$, $E > 0$, $k = i(-E)^{\frac{1}{2}}$, $E < 0$.   Defining a 2-sided Fourier transform of t thus:

$$t(\underline{p},\underline{q}) = \int d\underline{x} \; d\underline{y} \; \exp[i\underline{p}\cdot\underline{x} - i \; \underline{q}\cdot\underline{y}]t(\underline{x},\underline{y}) \quad (15.3)$$

and

$$t(\underline{x},y) = (2\pi)^{-6}\int d\underline{p} \; d\underline{q} \; \exp[-i\underline{p}\cdot\underline{x} + i\underline{q}\cdot\underline{y}]t(\underline{p},\underline{q}) \quad (15.4)$$

and appropriately transforming (15.1) the result is

$$t(\underline{p},\underline{q}) = v(\underline{p}-\underline{q}) + (2\pi)^{-3}\int d\underline{k} \; v(\underline{p}-\underline{k})G_o(\underline{k})t(\underline{k},\underline{q}) \quad (15.5)$$

Writing

$$t(\underline{p},\underline{q}) = \sum_{\ell m} t_\ell(pq)Y^*_{\ell m}(\theta_p\phi_p) \; Y_{\ell m}(\theta_q\phi_q) \quad (15.6)$$

and similarly for v $v(\underline{p}-\underline{q})$ the individual terms in the expansion of (15.5) are

$$t(pq) = v(pq) + (2\pi)^{-3} \int_0^\infty k^2 dk \; v(pk)G_o(k)t(kq) \quad (15.7)$$

The suffix ℓ has been dropped for convenience. $G_o^{\pm}(k)$ can be written

$$G_o^{\pm}(k) = [E-k^2]^{-1} \pm i\pi\delta(E-k^2) \quad (15.8)$$

16. Solution of the t matrix for continuum states (E > 0)

Separate t into its real and imaginary parts:

$$t(pq) = R(pq) + iI(pq) \tag{16.1}$$

Substituting (16.1) and (15.8) into (15.7) we get

$$R^+(pq) = v(pq) + (4\pi)^{-2} v(p\sqrt{E})\sqrt{E} I^+(\sqrt{E}q) + \int_0^\infty dk\, G(pkE) R^+(kq) \tag{16.2}$$

$$I^+(pq) = -(4\pi)^{-2} v(p\sqrt{E})\sqrt{E} R^+(\sqrt{E}q) + \int_0^\infty dk\, G(pkE) I^+(kq) \tag{16.3}$$

where $G(pkE) = (2\pi)^{-3} v(pk)k^2 \left[E-k^2\right]^{-1}$. Equations (16.2) and (16.3)

are of standard Fredholm type, and are solved by determination

of the inverse kernel to G(pkE), which satisfies the following

integral equation:

$$F(pkE) = G(pkE) + \int_0^\infty dk'\, G(pk'E)F(k'kE) \tag{16.4}$$

In terms of F, the solutions of (16.2) and (16.3) are

$$R^+(pq) = \omega(pq) + \omega(p\sqrt{E})\sqrt{E}\, I(\sqrt{E}q)(4\pi)^{-2} \tag{16.5}$$

$$I^+(pq) = -\omega(p\sqrt{E})\,\sqrt{E}\, R(\sqrt{E}q)(4\pi)^{-2} \tag{16.6}$$

where

$$\omega(pq) = v(pq) + \int_0^\infty F(pkE)\, v(kq) \tag{16.7}$$

Equations (16.5) and (16.6) can be separated by putting $p = \sqrt{E}$ in (16.6)

substituting into (16.5) and then putting $p = \sqrt{E}$ in (16.5) .

This gives $R(\sqrt{E}q)$ solely in terms of ω , and this expression

for $R(\sqrt{E}q)$ can be substituted back into (16.6).   The results are:

$$R^+(pq) = \omega(pq) - (4\pi)^{-4} E\, \omega(p\sqrt{E})\omega(\sqrt{E}\sqrt{E})\omega(\sqrt{E}q)$$

$$[1 + (4\pi)^{-4} E\omega(\sqrt{E}\sqrt{E})^2]^{-1} \tag{16.8}$$

$$I^+(pq) = -(4\pi)^{-2} \sqrt{E}\, \omega(p\sqrt{E})\omega(\sqrt{E}q)$$

$$[1 + (4\pi)^{-4} E\, \omega(\sqrt{E}\sqrt{E})^2]^{-1} \tag{16.9}$$

It is easily seen that $R^-(pq) = R^+(pq)$, $I^-(pq) = -I^+(pq)$.

17. The solution for $\rho'(r\ r'E)$

The double Fourier transform of $v(\underline{x})\,\delta(\underline{k}-\underline{y})$ according to eqn (15.3) is

$$v(\underline{p}-\underline{q}) = \int d\underline{x}\, \exp[i(\underline{p}-\underline{q})\cdot\underline{x}]\, v(\underline{x}) \tag{17.1}$$

Expanding both sides of equation (17.1) in spherical harmonics it is easy to see that:

$$v(pq) = (4\pi)^2 \int_0^\infty x^2\, dx\, v(x) j(px) j(qx) \tag{17.2}$$

so $v(pq) = v(qp)$. Expanding $\omega(pq)$ in a perturbation series by means of equations (16.7) and (16.4) it can be seen that every term is symmetric with respect to interchange of p and q. Hence, because of equation (17.2).

$$\omega(pq) = \omega(qp) \tag{17.3}$$

Hence also, from (16.8) and (16.9) $R(pq) = R(qp)$, $I(pq) = I(qp)$.

The relation between the t matrix and the Green function is:

$$G(\underline{x},\underline{y}) = G_0(\underline{x},\underline{y}) + \int d\underline{r}d\underline{r}' \, G_0(\underline{x},\underline{r}) t(\underline{r},\underline{r}') G_0(\underline{r}',\underline{y})$$

(17.4)

where G_o is given by equation (15.2). Double Fourier transform of yields:

$$G(pq) = (2\pi)^3 \, \delta(p-q)p^{-2} \, G_0(p) + G_0(p) t(\underline{p},\underline{q}) \, G_0(\underline{q})$$

(17.5)

Expanding (17.5) in spherical harmonics using equation the terms are:

$$G(pq) = (2\pi)^3 \, \delta(p-q)p^{-2} \, G_0(p) + G_0(p) t(pq) G_0(q)$$

(17.6)

Using the standard result that

$$\rho'(pqE) = i(2\pi)^{-1} \, [G^+(pqE) - G^-(pqE)]$$

(17.7)

and substituting (16.8) and (16.9) into (17.6), the result is

$$\pi\rho'(pqE) = (2\pi)^3 \, \delta(p-q)p^{-2} \, \pi\delta(E-p^2)$$

$$- \pi^2 \omega(p\sqrt{E})\sqrt{E}\omega(\sqrt{E}q) \delta(E-p^2) \delta(E-q^2) [1+(4\pi)^{-4}E\omega(\sqrt{E}/E)^2]^{-1}(4\pi)^{-2}$$

$$+\pi[\omega(pq)-(4\pi)^{-4}E\omega(p\sqrt{E})\omega(\sqrt{E}/E)\omega(\sqrt{E}q)[1+(4\pi)^{-4}E\omega(\sqrt{E}/E)^2]^{-1}]$$

$$x[\delta(E-p^2)(E-q^2)^{-1} + \delta(E-q^2)(E-p^2)^{-1}]$$

$$+(4\pi)^{-2}\sqrt{E}\omega(p\sqrt{E})\omega(\sqrt{E}q)[1+(4\pi)^{-4}E\omega(\sqrt{E}/E)^2]^{-1}[(E-p^2)(E-q^2)]^{-1}$$

(17.8)

From the expansion of equation (15.4) (applied to ρ') in spherical harmonics it is seen that:

$$(2\pi)^6(4\pi)^{-2}\rho'(rr'E)= \int_0^\infty p^2 dp q^2 dq \, j(pr) j(qr') \rho'(pqE)$$

(17.9)

Substituting (17.8) into (17.9) there results:

$$\rho'(rr'E) = \sqrt{E}\pi^{-1}[1+(4\pi)^{-4}E\; r'\sqrt{E}\sqrt{E})^2]^{-1}\; S(Er)S(Er')$$

where $\hspace{10cm}$ (17.10)

$$S(Er) = j(\sqrt{E}r)+(2\pi)^{-3}\int_0^\infty p^2 dp\; w(p\sqrt{E})j(pr)(E-p^2)^{-1}\hspace{1cm}(17.11)$$

and we have used equation (17.3). Thus the general form of ρ' is a product of a function of r and a function of r'. Defining

$$w(p\sqrt{E}) = (4\pi)^2\int_0^\infty r^2\; dr w(r\sqrt{E})j(pr)\;,\hspace{1cm}(17.12)$$

substituting equation (17.12) into (17.11) gives the result

$$S(Er) = j(\sqrt{E}r)+\int_0^\infty x^2\; dx w(x\sqrt{E})2\pi^{-1}\int_0^\infty p^2 dp\; j(px)j(pr)(E-p^2)^{-1}\hspace{1cm}(17.13)$$

The integral over p can be done by contours and the result is

$$S(Er) = j(\sqrt{E}r)+\sqrt{E}\int_0^\infty x^2\; dx\; j(\sqrt{E}r_<)n(\sqrt{E}r_>)\omega(x\sqrt{E})\hspace{1cm}(17.14)$$

where $r_<$ is the smaller of x and r, and $r_>$ the greater. Comparing (17.13) and (17.14) with the usual expression for the phase shift, it is easily seen that

$$\tan\eta(E) = -(4\pi)^{-2}\sqrt{E}\; w(\sqrt{E}\sqrt{E})\hspace{1cm}(17.15)$$

18. The solution for $\omega(pq)$

In coordinate space, equation (16.4) becomes

$$F(rr'E) = G(rr'E) + \int_0^\infty x^2\; dx\; G(rxE)F(xr'E)\hspace{1cm}(18.1)$$

where it is easily seen that

$$G(rr'E) = v(r)j(\sqrt{E}r_<)n(\sqrt{E}r_>) \qquad (18.2)$$

Defining a function $H(r\ r'E)$ as:

$$H(rr'E) = F(rr'E) / v(r) \qquad (18.3)$$

equation (18.1) becomes

$$H(rr'E) = \sqrt{E}j(\sqrt{E}r_<)n(\sqrt{E}r_<) + \sqrt{E}\int_0^\infty x^2 dx\, v(x)j(\sqrt{E}r_<)n(\sqrt{E}r_>)$$
$$H(xr'E) \qquad (18.4)$$

which can be seen to be equivalent to the differential equation

$$\left[\frac{1}{r^2}\frac{d}{dr}\ r^2\ \frac{d}{dr} + E - \frac{\ell(\ell+1)}{r^2} - v(r)\right] H(rr'E) = \frac{\delta(r-r')}{r^2} \qquad (18.5)$$

Thus $H(rr'E)$ is the real part of the single particle Green function in equation (17.4) and is the inverse kernel to $G(rr'E) = j(\sqrt{E}r_<)n(\sqrt{E}r_>)$ which solves the integral equation for the radial wave function:

$$R(Er) = j(\sqrt{E}r) + \int_0^\infty x^2 dx\, H(rxE)\ v(x)j(\sqrt{E}x) \qquad (18.6)$$

Using equns (16.7) together with eqn (17.11) it can be seen that

$$w(\sqrt{E}r) = v(r)\ R(Er) \qquad (18.7)$$

Substituting (18.7) into (17.11) and (17.10) gives the result

$$S(Er) = R(Er) \qquad (18.8)$$

Together with equation (17.15) this becomes

$$\rho'(rr'E) = \pi^{-1}\sqrt{E}\cos^2\eta(E)\ R(Er)\ R(Er') \qquad (18.9)$$

19. Friedel sum rule and idempotency of Dirac matrix

The Dirac matrix is obtained from ρ' by an integration over energy

$$\rho(\underline{r},\underline{r}'E) = \int_0^E dE' \; \rho'(\underline{r},\underline{r}',E) \qquad (19.1)$$

It is idempotent, i.e.

$$\rho(\underline{r},\underline{r}',E) = \int d\underline{x} \; \rho(\underline{r},\underline{x},E)\rho(\underline{x},\underline{r}', E) \qquad (19.2)$$

and obeys the closure relation

$$\rho(\underline{r},\underline{r}', \infty) = \delta(\underline{r}-\underline{r}') \qquad (19.3)$$

In equation (19.1) only the continuum states are considered. The bound state contribution, viz.

$$\rho_b(\underline{r},\underline{r}') = \sum_i \phi_i^*(\underline{r}) \; \phi_i(\underline{r}') \qquad (19.4)$$

must be added in before equation (19.3) is true. Here i runs over all the bound states of the system. If the scattering potential is to be completely screened at large distances, then the displaced charge must equal the net charge producing the potential, i.e.

$$\int d\underline{r} \; [\rho(\underline{r}\underline{r} \; E_f) - \rho_o(r,r,E_f)] = Z \qquad (19.5)$$

where E_f is the energy of the highest occupied state, and the region of integration is large. Expanding equations (19.1) to (19.5) in spherical harmonics it is seen that

$$\rho(rr'E) = \int_0^E dE^* \rho' \ (r \ r'E) \qquad (19.6)$$

$$\rho(rr'E) = \int_0^\infty x^2 dx \ \rho(rxE)\rho(xr'E) \qquad (19.7)$$

$$\rho(rr'\infty) = r^{-2}\delta(r - r') \qquad (19.8)$$

$$2.4\pi \sum_\ell \frac{(2\ell+1)}{4\pi} \int_0^R r^2 dr[\rho(rrE_f) - \rho_0(rrE_f)] = Z \qquad (19.9)$$

The factor of 2 in equation (19.9) accounts for spin degeneracy.
The radial wave function for continuum states satisfies the
di   ntial equation

$$\frac{d}{dr^2} r \ R(kr) + \left[k^2 - v(r) - \ell\frac{(\ell+1)}{r^2} \right] r \ R(kr) = 0 \qquad (19.10)$$

where $E = k^2$ and $rR(kr) = 0$ at $r = 0$. Multiplying (19.10) by
$\cos \eta(k)$, setting up a similar equation for $rR(k'r)$, subtracting,
integrating by parts gives

$$\int_0^R \left[[\cos\eta(k')rR(k'r)] \frac{d}{dr} [\cos\eta(k)rR(kr)] - [\cos\eta(k)rR(kr) \right.$$
$$\left. \frac{d}{dr}[\cos\eta(k') \ rR(k'r)] \right]$$
$$= (k'^2-k^2) \int_0^R r^2 dr \ \cos\eta(k)\cos\eta(k')R(kr)R(k'r)$$
$$\qquad (19.11)$$

The asymptotic form of R(kr) is

$$R(kr) = j(kr) - \tan\eta(k)\, n(kr) \qquad (19.12)$$

Hence, substituting $j(\rho) \to \rho^{-1}\cos[\rho-\frac{1}{2}(\ell+1)\pi]$,

$n(\rho) = \rho^{-1}\sin[\rho-\frac{1}{2}(\ell+1)\pi]$ and multiplying

by $\cos\eta(k)$ gives the result

$$\cos\eta(k)R(kr) = (kr)^{-1}\sin(kr + \eta(k) - \tfrac{1}{2}\ell\pi) \quad r \to \infty \qquad (19.13)$$

Substitution into (19.11) gives

$$\int_{0}^{R} r^2 dr\, \cos\eta(k)\cos\eta(k')\, k(kr)R(k'r) = \frac{1}{2kk'(k-k')}$$

$$\sin[(k-k')R+\eta(k)-\eta(k')] \qquad (19.14)$$

$$- \frac{1}{2kk'(k+k')}\sin[(k+k')R + \eta(k) +\eta(k') - \ell\pi]$$

which is the same thing as

$$\int_{0}^{R} r^2 dr\, \cos\eta(k)\cos\eta(k')R(kr)R(k'r)$$

$$= \frac{\pi}{2kk'}\left[\delta(k-k')\cos[\eta(k)-\eta(k')]\right.$$

$$\left.-\delta(k+k')\cos[\eta(k)+\eta(k')-\ell\pi]\right] + \frac{\cos(k-k')R}{2kk'(k-k')}\sin[\eta(k)-\eta(k')]$$

$$\qquad (19.15)$$

$$- \frac{\cos(k+k')R}{2kk'(k+k')}\sin[\eta(k)+\eta(k')-\ell\pi]$$

using the representation $\delta(x) = \underset{g \to \infty}{lim} \sin gx/\pi x.$ The
result for free electrons obtains by setting $\eta = 0.$

Hence

$$\int_0^R r^2 dr[\rho'(rr'k) - \rho_o'(rr'k)]$$

$$= \frac{1}{2k^2} \underset{k' \to k}{lim} \frac{\sin[\eta(k) - \eta(k')]}{k-k'} + \text{an oscillating term.} \tag{19.16}$$

But since $\eta(k') = \eta(k) + (k'-k) \, d\eta/dk$ and neglecting the
oscillatory term:

$$\int_0^R r^2 dr[\rho'(rr'k) - \rho_o'(rr'k)] = \frac{d\eta/dk}{2k^2} = \frac{1}{\sqrt{E}} \frac{d\eta}{dE} \tag{19.17}$$

Hence using (18.9) and (19.9) we obtain the result

$$\frac{2}{\pi} \overline{\sum_\ell} (2\ell+1) \, \eta(E_f) = Z \tag{19.18}$$

which is just the Friedel sum rule. To prove that the solution (17.15)
produces an idempotent Dirac matrix, using (19.6) and (19.7) we obtain

$$\rho(rr'E) = \frac{1}{\pi^2} \int_0^k 2k'^2 \, dk' 2k''^2 dk'' \cos\eta(k') \cos\eta(k'') R(rk')$$

$$R(r'k'')$$

$$x \int_0^\infty x^2 dx \cos\eta(k') \cos\eta(k'') R(xk') R(xk'') \tag{19.19}$$

which is to be proved, if the solution is idempotent. The last factor in equation (19.19) is given by equation (19.15). Notice first that the term in $\delta(k'+k'')$ does not contribute, since k'' and k'' are always greater than 0. Secondly, the oscillatory terms also give zero contribution as $R \to \infty$, since the integrands are smooth functions of k' and k''. The only part where care is required is the vanishing denominator in

$$\frac{\cos(k-k')R}{2kk'} \frac{\sin[\eta(k)-\eta(k')]}{k-k'} \quad \text{when } k' \to k$$

But as (19.6) and (1917) show, this gives rise to no difficulty. Hence

$$\int_0^\infty x^2 dx \cos\eta(k')\cos\eta(k'')R(xk')R(xk'') = \frac{\pi}{2k^2} \delta(k-k') \quad (19.20)$$

and so the right hand side of equation (19.19) becomes

$$\frac{1}{\pi} \int_0^k 2k'^2 \, dk' \cos\eta(k')\cos\eta(k') \, R(rk')R(r'k')$$

which is just $\rho(rr'E)$, by equations (17.15) and (19.6). Adding in the bound state contribution to ρ gives no difficulty, as this part is idempotent in itself, and integrals of products of ϕ and R vanish, as these functions are orthogonal.

20. Proof of closure relation

Expand an arbitrary function $\psi(r\,r')$ in the function $\rho'(rr'E)$ and the bound state wave functions $\phi_i(r)$ (we write $\phi_i(r)$ for the ℓth component of $\phi_i(r)$, for simplicity). Then

$$\psi(rr') = \sum_1 C_1 \phi_1(r)\phi_1(r') + \frac{1}{\pi^2} \int_0^\infty 2k^2 dk\; 2k'^2 dk' \cos\eta(k)$$

$$\cos\eta(r') R(kr)R(k'r')\theta(kk') \qquad (20.1)$$

Now multiply (20.1) by $\pi^{-1} \cos\eta(k'')\cos\eta(k''')R(k''r)R(k'''r')$ and integrate over r, r'. We have

$$\frac{1}{\pi} \int_0^\infty r^2 dr r'^2 dr'\; \psi(rr')\cos\eta(k'')\cos\eta(k''')R(k''r)R(k'''r')$$

$$= \frac{1}{\pi^3} \int_0^\infty 2k^2 dk 2k'^2 dk' r^2 dr r'^2 dr' R(kr)\cos\eta(k)R(k''r)\cos\eta(k'')$$

$$x\; R(k'r')\cos\eta(k')R(k'''r')\cos\eta(k''')\; \theta(kk') \qquad (20.2)$$

because of the orthogonality of R and ϕ. Because of equ. (19.12) we have

$$\int_0^\infty r^2 dr r'^2 dr'\psi(rr')\cos\eta(k'')R(k''r)\cos\eta(k''')R(k'''r')$$

$$= \theta(k''k''') . \qquad (20.3)$$

Now set $k''=k'''$ and integrate over k''. We have then

$$\int_0^\infty r^2 dr r'^2 dr'\psi(rr')\; \frac{1}{\pi} \int_0^\infty 2k^2 dk\; \cos\eta(k)R(kr)\cos\eta(k)R(kr')$$

$$= \frac{1}{\pi} \int_0^\infty 2k^2 dk\theta(kk) \qquad (20.4)$$

But from

$$\int_0^\infty r^2 dr\psi(rr) = \sum_1 C_1 + \frac{1}{\pi^2} \int_0^\infty 2k^2 dk 2k'^2 dk' \frac{\pi}{2k'^2}$$

$$\delta'k-k')\theta(kk') \qquad (20.5)$$

$$\therefore \int_0^\infty r^2 dr\psi(rr) = \sum_1 C_1 + \frac{1}{\pi} \int_0^\infty 2k^2 dk\theta(kk)$$

Comparing (20.4) and (20.5) we see that we must have

$$\frac{1}{\pi} \int_0^\infty 2k^2 dk \cos\eta(k)R(kr)\cos\eta(k)R(kr')$$

$$= \frac{\delta(r-r')}{r^2} - \sum_i \phi_i(r)\phi_i(r') \tag{20.6}$$

Hence the solution given in equation (18.9) together with the bound state contribution, satisfies the closure relation, as well as idempotency and the Friedel sum rule.

21. <u>Summary</u>

Part A has reported a treatment of relaxations round point defects in metals, using electron theory. Preliminary results are reported for Ag in Li and for a vacancy in Cu, and further work is in progress on applications of this theory.

In Part B, our earlier work on electron states is extended to deal with the electrical resistivity of liquid metals where there is strong electron scattering. The theory should be applicable to liquid metals like calcium and barium, which have relatively high resistivity and numerical calculations on calcium are in progress, using the method outlined immediately above for treating the single-centre scattering from a calcium ion. Generalizations to liquid metal alloys are also under investigation.

Appendix 1

Relations between functions F, R and P characterizing

perfect lattice

We want to summarize here some of the basic properties of the functions F, $\underset{\sim}{R}$ and $\underset{\sim}{P}$ which, in principle, can be found from the theory of the perfect crystal. To obtain F, as stressed above, is a one-body problem, once the potential $V_p(\underline{r})$ is known. On the other hand, exact determination of $\underset{\sim}{R}$ and $\underset{\sim}{P}$ is not possible at present, as these quantities depend on the exchange and correlation energy of an inhomogeneous electron gas.

Proof of relation (3.4) between response

function F and one-body Green function and density

matrix

As remarked above, the relation (3.4) was given by Stoddart, March and Stott (1969). An elementary proof of this will be sketched below.

Eqn. (3.7) gives us the change in the Bloch density matrix $C_o(\underline{r}\ \underline{r}'\ \beta$) due to a change in potential ΔV, a change we denote by $\Delta C(\underline{r}\ \beta$) on the diagonal.

Then we have immediately from eqn. (3.7) that

$$\Delta C(\underline{r} \ \beta) = -\int d\underline{r}' \ \Delta V(\underline{r}')\int_0^\beta d\beta_1 \ C_0(\underline{r} \ \underline{r}'\beta - \beta_1) \ C_0(\underline{r}'\underline{r} \ \beta_1).$$

$$(A1.1)$$

We now compare this result with the density change $\Delta\rho \ (\underline{r} \ E)$ caused by the same change in potential. This, from eqn. (4.11) with $V_d(r)$ set equal to zero is

$$\Delta\rho(\underline{r} \ E) = \int d\underline{r}' \ \Delta V(\underline{r}') \ F(\underline{r} \ \underline{r}' \ E).$$

$$(A1.2)$$

But we have the Laplace transform relation between C and ρ (provided we add a positive potential energy to bring all energies ≥ 0)

$$\Delta C(\underline{r}\beta) = \beta\int_0^\infty \Delta\rho \ (\underline{r} \ E) \ e^{-\beta E} \ dE.$$

$$(A1.3)$$

Integrating this equation by parts, we find

$$\Delta C(\underline{r} \ \beta) = \int_0^\infty e^{-\beta E} \frac{d}{dE} \ \Delta\rho(\underline{r}E)dE$$

$$(A1.4)$$

$$= \int d\underline{r}' \ \Delta V(\underline{r}') \int_0^\infty e^{-\beta E} \frac{\partial F(\underline{r} \ \underline{r}' \ E)}{\partial E} \ dE$$

where the last line follows by differentiating eqn. (A1.2) with respect to E.

It is clear then from eqns (A1.1) and (A1.4) that $\partial F/\partial E$ can be related to the integral over β_1 of the product of C_0's displayed explicitly in eqn. (A1.1). Substituting

the explicit form (3.1) for C_o, the β_1 integration is readily accomplished.   Similarly, the inverse Laplace transform required to obtain $\partial F/\partial E$ from equ. (A1.4) is easily completed.   Hence, using the explicit definitions of C_o and ρ_o, eqn. (3.4) follows.

Integral equation for $\underline{R}$

The determination of $\underline{R}$ from first principles presents more difficulty, though a semi-empirical procedure can be devised to obtain a useful starting approximation (see Appendix 3).

The argument sketched below follows the discussion of JM and is given for completeness in that the potential $\Delta V(\underline{r})$ required to generate the Kanzaki lattice depends on $\underline{P}$ through eqn. (3.2). The essential point is that we can write the change in the one-body potential as we move the ions from $\underline{\ell}$ to $\underline{\ell} + \underline{u}_\ell$ as

$$\Delta V = \Delta V_{elect\ ostatic} + \int U(\underline{r}\ \underline{r}')\rho_1(\underline{r}')\ d\underline{r}'. \quad (A1.5)$$

But ρ_1 is related to $\underline{R}\ (\underline{r})$ and we also have

$$\Delta V = \sum_\ell \int \frac{\underline{u}_\ell \cdot \underline{R}\ (\underline{r}' - \underline{\ell})d\underline{r}'}{|\underline{r} - \underline{r}'|} + \sum_\ell \left[\frac{Ze}{|\underline{r} - \underline{\ell} - \underline{u}_\ell)} - \frac{Ze}{|\underline{r} - \underline{\ell}|} \right.$$

$$+ \sum_\ell \underline{u}_\ell \cdot \int U(\underline{r}\ \underline{r}')\ \underline{R}(\underline{r}' - \underline{\ell})\ d\underline{r}' \qquad (A1.6)$$

This can now be expanded to $O(\underline{u}_{\ell})$ to yield the form (.3.2)

where

$$\underline{P}(\underline{r}) = \int \frac{\underline{R}(\underline{r}')d\underline{r}'}{|\underline{r} - \underline{r}'|} - \frac{Ze\ \underline{r}}{r^2} + \int U(\underline{r}\ \underline{r}')\ \underline{R}\ (\underline{r}')d\underline{r}'$$

$$(A1.7)$$

After some manipulation, the basic integral equation (3.3)

of JM then follows.

Appendix 2

To avoid the troublesome problem of solving eqn. (4.2) by numerical iteration, we shall now argue as follows. With the defect potential $V_d(r)$ introduced into the **perfect** lattice, let us suppose that by the methods of Stoddart, March and Stott (1969) we have generated a density matrix C_u, where u stands for the unrelaxed defect lattice. Then we define

$$\Delta C_{uo} = C_u - C_o \qquad (A2.1)$$

and

$$\Delta C_{fK} = C_f - C_K. \qquad (A2.2)$$

It seems reasonable to assume that a useful starting point for the calculation of ΔC_{fK} would be ΔC_{uo}, which, at least, includes the full effect of the defect potential $V_d(r)$, though **not**, at first, the relaxations.

It is now a simple matter to show, from the integral form of the Bloch equation, that

$$\Delta C_{fK} = -\int_0^\beta d\beta_1 \int d\underline{r}'' \left\{ \left(\Delta C_{fK}(\underline{r}\ \underline{r}''\ \beta - \beta_1) + C_{fK}(\underline{r}\ \underline{r}''\beta-\beta_1) \right) \right.$$

$$\left. V_d(\underline{r}'')\ C_K(\underline{r}''\underline{r}'\ \beta_1) \right\} \qquad (A2.3)$$

and

$$\Delta C_{uo} = -\int_0^\beta d\beta_1 \int d\underline{r}'' \left[\left(\Delta C_{uo}(\underline{r}\ \underline{r}''\beta-\beta_1) + C_{uo}(\underline{r}\ \underline{r}''\beta-\beta_1) \right) \right.$$

$$V_d(\underline{r}'')\ C_o(\underline{r}''\ \underline{r}'\ \beta_1). \tag{A2.4}$$

Subtracting these, we have for the error $\delta C = \Delta C_{fK} - \Delta C_{uo}$ the result

$$\delta C = -\int_0^\beta d\beta_1 \int d\underline{r}'' \left[\delta C + \Delta C_{uo} + C_K \right] V_d(\underline{r}'') C_K(\underline{r}''\ \underline{r}'\beta_1)$$

$$+ \int_0^\beta d\beta_1 \int d\underline{r}'' \left[\Delta C_{uo} + C_o \right] V_d(\underline{r}'')\ C_o(\underline{r}''\ \underline{r}'\ \beta_1). \tag{A2.5}$$

Now we have also

$$C_K - C_o = C_{Ko} \tag{A2.6}$$

where ΔC_{Ko} is $0(\underline{u}_\ell)$. Thus to $0(\underline{u}_\ell)$ we find

$$\delta C = -\int_0^\beta d\beta_1 \int d\underline{r}'' \left[\delta C + \Delta C_{Ko} \right] V_d(\underline{r}'')\ C_o(\underline{r}''\ \underline{r}'\beta_1)$$

$$-\int_0^\beta d\beta_1 \int d\underline{r}'' \left[\Delta C_{uo} + C_o \right] V_d(\underline{r}'')\ \Delta C_{Ko}(\underline{r}''\underline{r}'\beta_1). \tag{A2.7}$$

If we further assume, as starting point, that $\delta C < \Delta C_{Ko}$ then we have as the first approximation to correct the charge 'displaced' by $V_d(\underline{r}_1)$ in the unrelaxed crystal

$$\delta C \simeq -2\int_0^\beta d\beta_1 \int d\underline{r}'' \Delta C_{Ko}\ V_d(\underline{r}'')\ C_o(\underline{r}''\ \underline{r}'\ \beta_1)$$

$$-\int_0^\beta d\beta_1 \int d\underline{r}'' \Delta C_{uo}\ V_d(\underline{r}'')\ \Delta C_{Ko}(\underline{r}''\ \underline{r}'\ \beta_1). \tag{A2.8}$$

Here then, is an expression to correct the displaced charge
for the effects of relaxation, in terms of the properties of the
unrelaxed crystal containing the defect potential $V_d(\underline{r})$.

To get a self-consistent theory, it is clear that eqn. (4.10)
must be used to refine the displaced charge in the unrelaxed crystal.
If we work with the Green function, the β integration in (4.10)
is immediately removed.

It may well be possible to calculate local changes around
the vacancy by making the additional approximation in eqn. (4.10)
that τ_d varies slowly in space. Then for the diagonal element
$\delta C(\underline{r}\ \underline{r}\ \beta)$ we find

$$
\delta C(\underline{r}\ \underline{r}\ \beta) \simeq
$$
$$
- V_d(\underline{r}) \int_0^\infty d\beta_1 \int d\underline{r}'' \left[\Delta C_{Ko}\ (\underline{r}\ \underline{r}'\ \beta_1) \right.
$$
$$
\left\{ 2C_o\ (\underline{r}''\ \underline{r}\ \beta - \beta_1) \right. \qquad (A2.9)
$$
$$
\left. \left. + \Delta C_{uo}(\underline{r}''\ \underline{r}\ \beta - \beta_1) \right\} \right.
$$

In the main report we give a rather cruder form of eqn. (A2.9).
Clearly, however, eqn. (A2.7) provides a perfectly proper
starting point for refining the displaced charge calculated
in the unrelaxed lattice.

Appendix 3

Preliminary estimate of $\rho_1(\underline{r})$, the charge 'displaced'

in the Kanzaki lattice, for vacancy in Cu

Since the evaluation of the displaced charge in the presence of relaxation is, via eqn. (4.11), intimately related to the charge displaced in Kanzaki lattice, namely $\rho_1(\underline{r})$, we have made some preliminary estimates of this quantity for a vacancy in Cu.

Evidently, to calculate $\rho_1(\underline{r})$ from eqn. (2.1), we must have information on the displacements $\underline{u}_\ell$ and the response function $\underline{R}(\underline{r})$.

Tewordt (1958) has dealt with the problem of the relaxations round a vacancy in Cu by matching local relaxations around the vacancy, obtained using Born-Mayer pair potentials, on to the long-range relaxations which can be properly treated by replacing the discrete crystal by a continuum. This approximation becomes valid outside a sufficiently large region enclosing the defect or defect complex. For then the displacements $\underline{u}_\ell$ become small and vary slowly from atom to atom.

We have used these displacements $\underline{u}_\ell$ as given by Tewordt (1958), even though they will eventually need

refining to take account of the detailed nature of the
displaced charge round the vacant site as discussed in this
report.

It only then remains to set up a suitable approximation
to $R(\underline{r})$ in eqn. (2.1). We already have the Fourier
components $R_{\underline{K}}$ at the reciprocal lattice vectors $\underline{K}$ through
eqn. (2.3). Batterman, Chipman and de Marco ((1961)
have studied the X-ray scattering from Cu and we therefore have .
approximate estimates available of the ρ_K's. Following JM,
we have made the assumption that we can use the form (2.3)
for all $\underline{k}$, smoothly interpolating between the $\rho_{\underline{K}}$'s at the
reciprocal lattice vectors to obtain $\rho_{\underline{k}}$. Obviously this
procedure is not unique and eventually the integral equation
of JM (see Appendix 1) must be solved to find $\underline{R}(\underline{r})$.

The above assumption, as emphasized by JM, is equivalent
to the assumption of pair forces, and we can then write $\underline{R}$
as the gradient of a scalar density $\sigma(r)$, namely

$$\underline{R}\;(\underline{r})\;=\;\nabla\sigma(\underline{r}) \tag{A3.1}$$

where, from eqn. (2.2) it then follows that

$$\rho_0(\underline{r})\;=\;\sum_{\underline{\ell}}\sigma(\underline{r}\;-\;\underline{\ell}). \tag{A3.2}$$

Provided $\sigma(\underline{r})$ has the correct Fourier components at the
reciprocal lattice vectors, which is of course ensured by our
procedure to within the accuracy of the experimental measurements,

then eqn. (A3.2) will reproduce the exact ground-state
charge density of the crystal.

The form of σ used to fit the X-ray results of Batterman
et al is given (cf. Jones, March and Tucker, 1965) in Figs Al - A3.

Displaced charge in Cu metal

As an example, we shall compute the displaced charge in
Cu metal using Tewordt's displacements and making the prelim-
inary approximation $\underline{R} = \nabla \sigma$.   We fit σ the 'pseudoatom'
charge density to the X-ray scattering experiments as shown. ..
in Figs Al and A2.

Using the Hartree-Fock atom density as starting point,
the correction $\Delta\sigma$ (k) required to fit the X-ray scattering
at the Bragg reflections is shown explicitly in Fig Al.
This is not unique; we have simply drawn a smooth curve
through the measurements, and, of course, eventually the
integral equation of Jones and March will have to be used to
find $\underline{R}(\underline{r})$.   The Fourier transform $\Delta\sigma(\underline{r})$ is shown in Fig A2.

We then calculate

$$\rho_1(\underline{r}) = \sum_{\ell} \underline{u}_\ell \cdot \quad \nabla\sigma(\underline{r} - \underline{\ell}) \qquad (A3.3)$$

for various directions in the crystal and the results are
shown in Figs. A3-A5.   The very marked anisotropy evident
there is a consequence of the fact that as we go out along
the< 111> direction we do not encounter an atom over the
range shown.   This then is a first estimate of the charge
displaced in the Kanzaki lattice, strained to account for
the displacements round a vacancy in Cu.

Appendix 4

Relation between response function approach and elasticity theory in long wavelength limit

The customary elasticity approach gives us the result that, in response to a localized body force, which in $\underline{k}$ space, in the long wavelength limit gives us the Fourier transform of the force F in the form

$$\underline{F}\,(\underline{k}) = i\,\underline{k}\,\lambda \qquad (A4.1)$$

where λ measures the strength of the body-force, the displacements $\underline{u}_\ell\,(\underline{r})$ take the form

$$\underline{u}_\ell\,(\underline{r}) = \frac{c\,\underline{r}}{r^3} \qquad (A4.2)$$

The multiplying constant in eqn. ($A4.2$) is determined in Tewordt's method by matching to the 'discrete' displacements in the immediate neighbourhood of the defect.

It is evident in Kanzaki's method that F and u are related by the dynamical matrix $D_{\alpha\beta}$ $(\underline{k})$, which in turn, as JM discuss, is related to the response function $\underline{R}(\underline{r})$. It then becomes clear that elasticity theory gives us rather direct information on the response function $\underline{R}(\underline{k})$ at small $\underline{k}$, and, in particular relates the small $\underline{k}$ behaviour rather directly to the elastic constants. This will be discussed quantitatively elsewhere by Claesson, Jones and March (to be published) in connection with many-body forces in lattice dynamics.

We want only to make one other point relating to
elasticity theory here.   Corresponding to the displacements
(A4.2), it is well known that there is a volume change
per defect given by

$$\Delta \Omega = 4\pi c \gamma \qquad\qquad (A4.3)$$

where $\gamma = 3(1 - \sigma)/(1 + \sigma)$, σ being Poisson's ratio.
We anticipate that eventually it may be necessary to check
that the defect potential adopted obeys some condition equivalent
to a Friedel sum rule into which the volume change (A4.3   )
is incorporated, as we indicated in the Introduction.   Our
microscopic theory is not yet sufficiently well developed to
give a precise understanding of this point, which is worth
further study.

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Captions for Figures

Fig. 1.   Local density of states $\sigma(\underline{r}\ E)$ for Mg in Li (solid curve) for $E = \frac{1}{2}\ E_f$.   Dashed curves show local density of states in pure Mg and pure Li metal.

Fig. 2.   As in Fig. 1 but for $E = E_f$(private communication from J. Inglesfield).

Fig. 3.   Total displaced charge $Q(r)$ inside sphere of radius r in case of vacancies in Cu $(Z = -1)$, Mg$(Z = -2)$, Aℓ $(Z = -3)$ and Pb $(Z = -4)$.

This is needed to calculate electric field in Kanzaki lattice.   Results shown are from the work of Stott, Baranovsky and March (1970;   see also March and Stoddart (1968; p.551)).

Fig. A.1. $\Delta\sigma$ versus $(h^2 + k^2 + \ell^2)^{\frac{1}{2}}$ for Cu, used to fit X-ray results of Batterman et al.   Form is given by

$$\Delta\sigma(K) = A_1 K_3^{-a_1 K} + A_2 K^7\ e^{-a_2 K}$$
$A_1 = 3.24,\ a_1 = 1.11, A_2 = 0.0083,\ a_2 = 1.35.$

Fig. A.2. $\Delta\sigma$ (r) corresponding to $\Delta\sigma$ (K) in Fig. A.1.

Fig. A.3.   Charge density ρ_0 in Cu, together with displaced charge ρ_1 in Kanzaki lattice when strained by a vacancy.   Densities shown along <100> direction.

Fig. A.4.   Same as Fig. A.3. but along <110> direction.

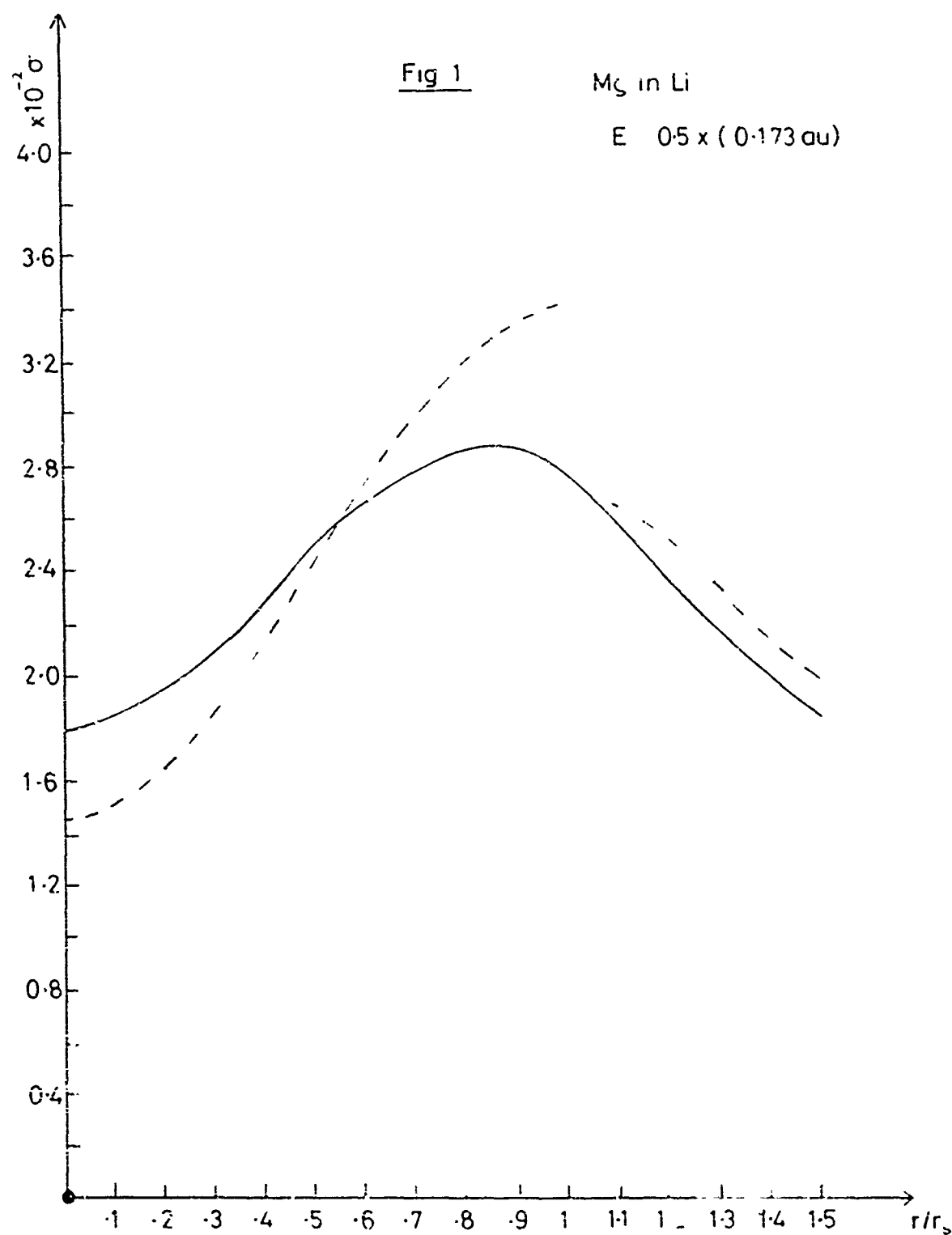Fig. A.5.   Same as Fig. A.3. and A.4. but along <111> direction.

Fig 1   Mg in Li

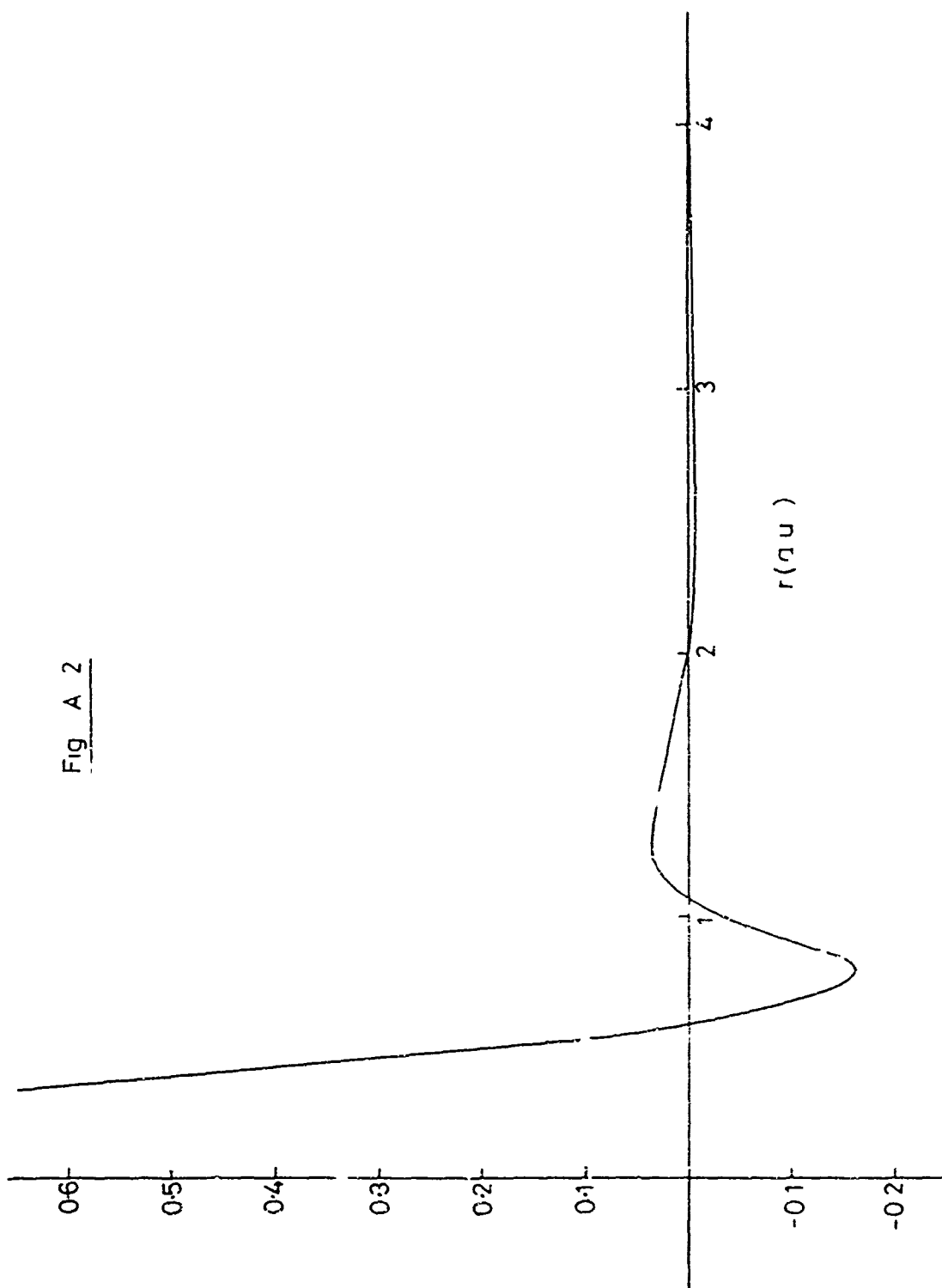E   0·5 x (0·173 au)

Fig 2   Mg in Li

E = 0·173 au

Fig 3

Fig A1

Fig A 2
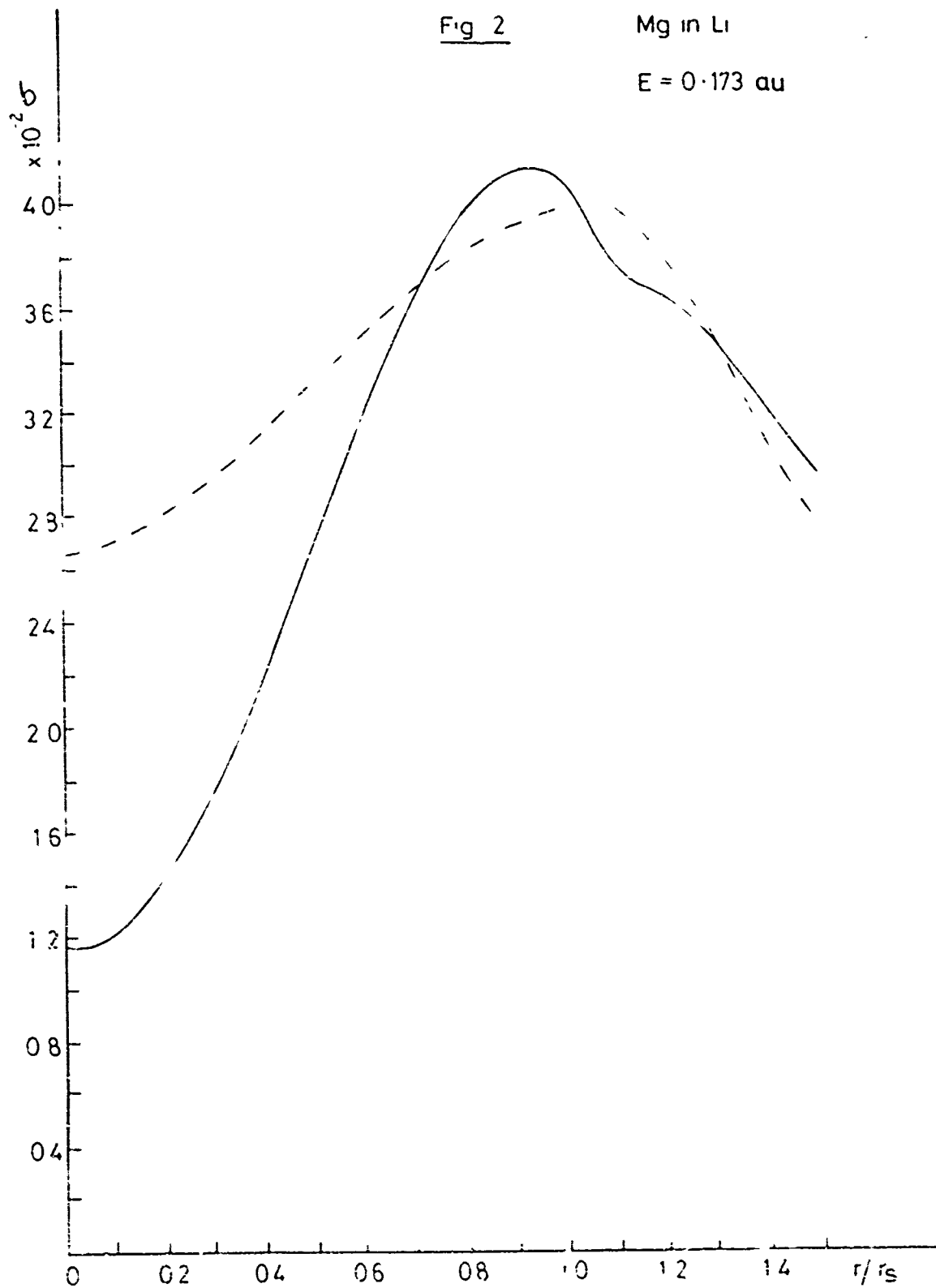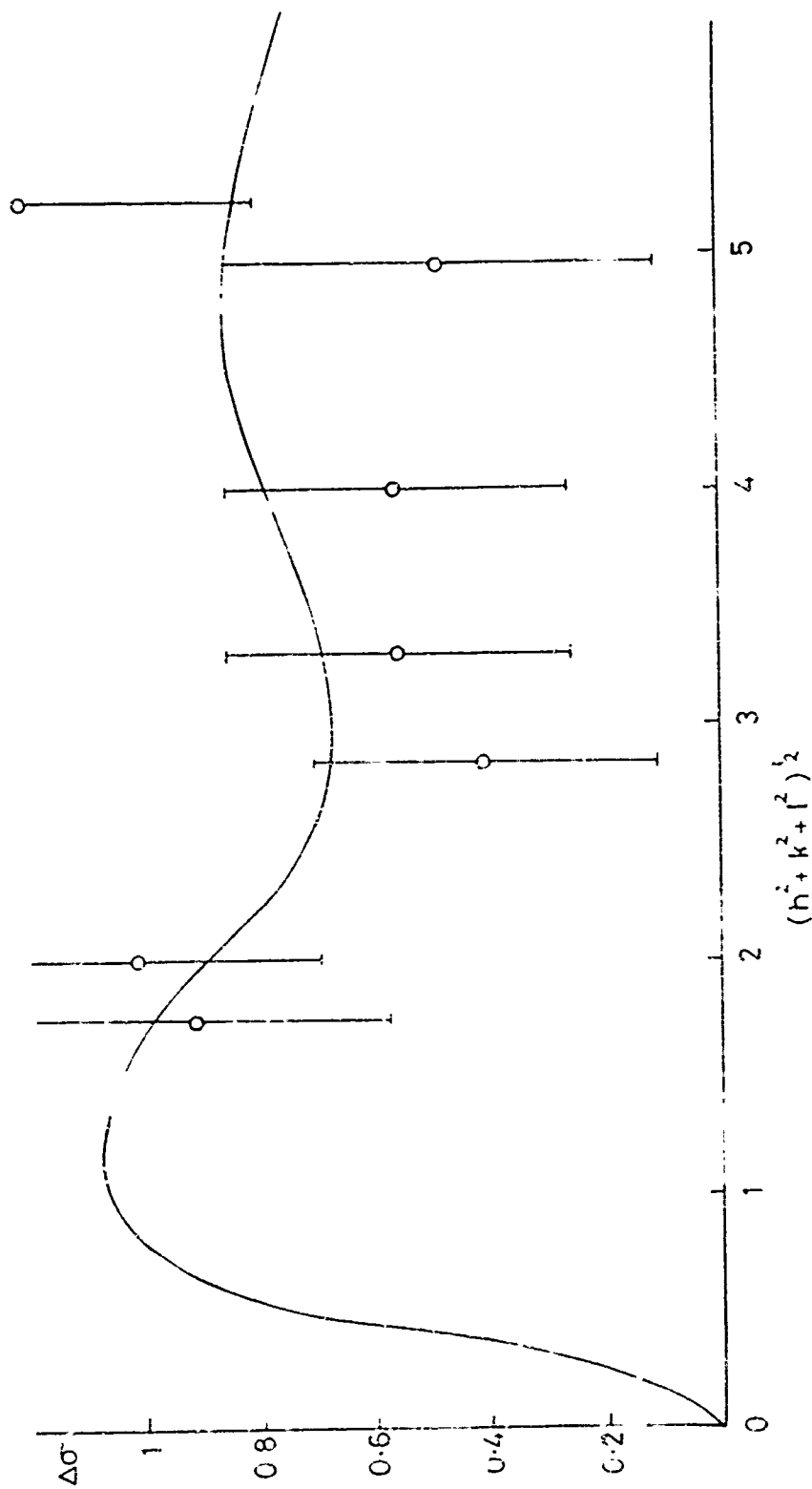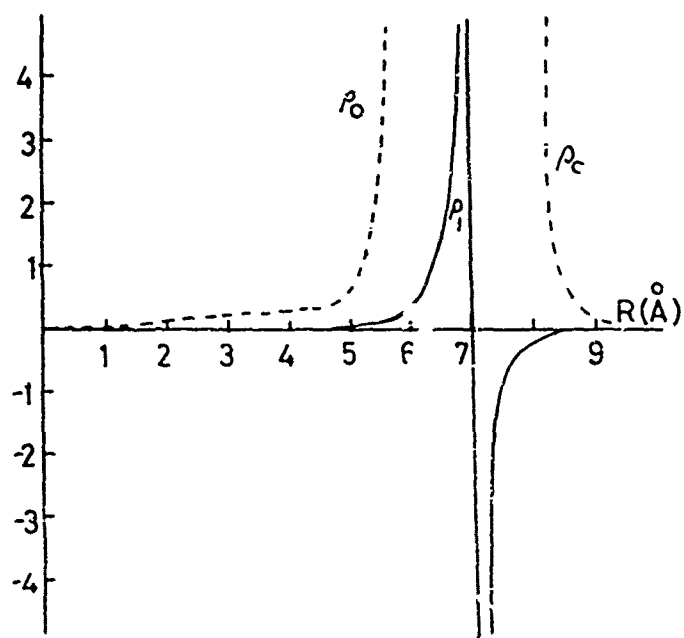
Fig A.3

a Along <100> Direction
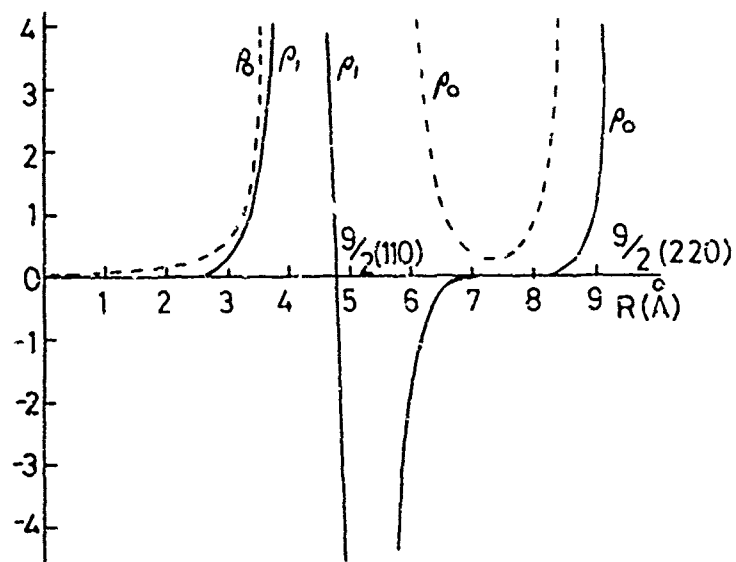
Fig A 4

b Along <110> Direction
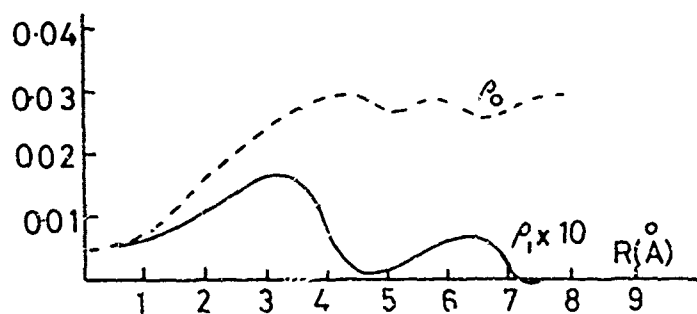
Fig A5

c Along <111> Direction